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REPORT S-114

NFPA-ACRYLIC ACID COPOLYMERIZATION CHARACTERISTICS AND
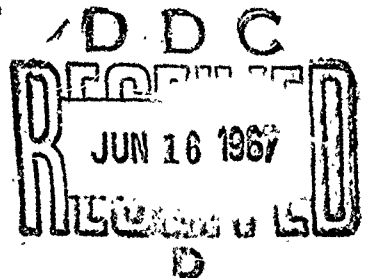PROCESS DEVELOPMENT (U)

by

D. A. Willoughby

June 1967

U. S. ARMY MISSILE COMMAND
CONTRACT DA-01-021 AMC-11536(Z)

ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807

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June 1967   Report S-114

NFPA-ACRYLIC ACID COPOLYMERIZATION CHARACTERISTICS AND PROCESS DEVELOPMENT (U)

by

D. A. Willoughby

U.S. ARMY MISSILE COMMAND
Contract DA-01-021 AMC-11536(Z)

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(U) ABSTRACT

This report discusses continued efforts to improve the process for making NFPA-acrylic acid copolymers and to characterize the product. Particular emphasis is directed toward developing, experimentally testing, and utilizing mathematical models of the process. The scope of the work includes considerations of compositional uniformity, molecular-weight distribution, and polymerization rate of the copolymer. A new process whereby the comonomers are added incrementally is described which greatly increases the productivity of the reactor and permits control of molecular weight. Propellant made from copolymer prepared in this manner has improved physical properties, fissuring characteristics, and physical-property aging characteristics.

(U) FOREWORD

The assistance and contributions of M. G. Baldwin,
D. W. Booth, E. D. Bosserman, K. E. Johnson, and B. K. Nipp
are gratefully acknowledged.

(U) CONTENTS

1.0   INTRODUCTION

Practical utilization of NFPA[1] as a high-energy binder for solid propellants has necessitated the use of the prepolymer approach for making the polymer. This approach is required because the polymerization reaction is highly exothermic, results in considerable shrinkage, and is difficult to control if the reaction is carried out in a propellant slurry. However, if NFPA is copolymerized in a suitable reactor, with another monomer containing a functionality permitting crosslinking when incorporated in the propellant slurry, the exotherm and shrinkage problems can be easily accommodated. In addition, process conditions in the reactor can be easily controlled and duplicated to produce a copolymer with consistent compositional uniformity, molecular weight distribution, and other related characteristics.

Previous work at these Laboratories [1, 2, 3] has led to the selection of acrylic acid (AA) as the comonomer to be used with NFPA, ethyl acetate (EtOAc) as the solvent for the reaction, and benzoyl peroxide (BPO) as the initiator. The work covered in this report extends this work with particular emphasis in developing, experimentally testing, and utilizing mathematical mode's of the process. The scope includes considerations of compositional uniformity, molecular-weight distribution, and polymerization rate of the copolymer.

A new process for making NFPA-AA copolymer was developed as a part of this effort, significantly increasing the productivity of the reactor and permitting control of the molecular weight. Propellant made from copolymer prepared by this new process has superior physical properties and fissuring characteristics.

2.0   EXPERIMENTAL PROCEDURES AND RESULTS

Experiments to measure reactivity ratios and polymerization rates were carried out on a small scale behind shields using 20 gm or less of monomer. A sketch of the reactor used in the experiments is shown in Fig. 1.

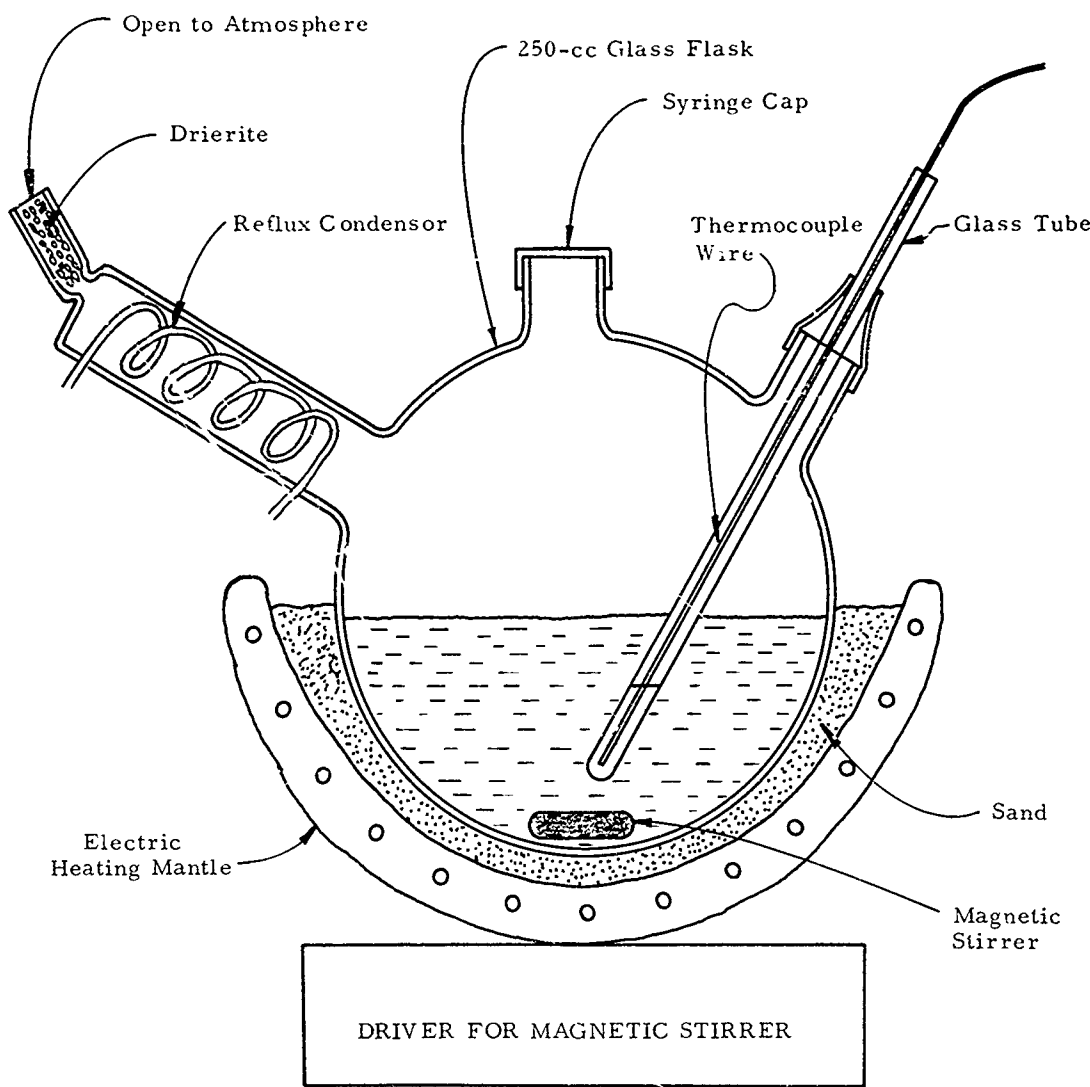[1]NFPA: 2, 3-bis(difluoramino)propyl acrylate

Fig. 1 Sketch of Experimental Setup

The reactor, which was operated under total-reflux conditions at atmospheric pressure, was formed from a 250-cc. three-neck Pyrex®[*] flask. The reactor rested in a sand-filled heating mantle which sat on top of a driver for a magnetic stirrer. The center neck was covered with a syringe cap. A glass, water-cooled reflux condenser fit in one side of the flask and a glass-covered thermocouple probe fit in the other side. Thirty-gauge copper-constantan thermo-couple wire was used in the probe. A Teflon®[**]-covered stirring bar was placed in the vessel. The reaction solution consisted of a mixture of EtOAc solvent, the NFPA and AA comonomers, and the BPO initiator. Approximately 2-cc of 60-mesh Teflon powder was added for a normal charge of solution (about 150 cc) to serve as boiling chips. The Teflon powder is non-abrasive, which is desirable since one of the monomers is explosive, and proved to be more effective than glass beads in minimizing superheating in the liquid phase. During an experiment, the solution was stirred with the magnetic stirrer. A reference flask similar in all respects but containing only EtOAc and Teflon powder was also used so that the boiling-point elevation of the reactor solution could be measured. The thermocouple wires from both probes led to nearby mercury-filled glass tubes which were immersed in an ice bath containing finely ground crushed ice in water. Larger copper lead wires led from the ice bath through a three-way, low-thermal-EMF switch to a Leeds and Northrup[1] K-3 potentiometer. The K-3 potentiometer has a guaranteed accuracy of ±0.5 microvolt which represented about 0.01°C in this experimental setup.

Temperature histories of both the reactor and the reference flask were obtained. The temperature difference was measured by first obtaining a hand-smoothed plot of the temperature history of each solution, and then subtracting the temperature of the reference

---

[*]
[**] Trademark of Corning Glass Works, 80 Houghton Park, Corning, N.Y.
Trademark of E. I. duPont deNemours and Company, Wilmington, Del.
[1] Leeds and Northrup Company, Rockland and Stenton Avenues. Philadelphia, Pa.

solution from the reactor solution. This technique was found to be
superior to the use of a differential thermocouple arrangement to
measure the temperature difference directly. The temperature
difference was measured to an accuracy of about 0.10°C and a pre-
cision of about 0.05°C, a judgment based on the following observa-
tions: (1) For the described conditions the thermocouple readings
were unaffected by the addition of more Teflon powder or by increasing
the stirring beyond the moderate level used. (2) When only solvent
and Teflon powder were placed in both vessels under reflux conditions,
the temperatures were repeatedly within 0.05°C of each other when
smoothed temperatures were compared. (3) Short-term temperature
fluctuations of approximately 0.05°C were observed in both the reactor
and the reference flask.

In conducting the experiments to determine reactivity ratios,
weighed amounts of solvent and comonomers were added to the reactor
vessel, the reference flask was filled with solvent to a comparable
level, and Teflon powder was added to both vessels. Next, a 3-cc
sample of reactor solution was obtained with a hypodermic syringe
and placed in a 4-cc 1.2-in. diameter glass vial which contained
a small amount of diphenylpicrylhydrazyl inhibitor. The sample was
capped with a polyethylene cap, cooled in an ice bath, and placed in a
refrigerator to await gas-chromatograph (GC) analysis. After this
initial sample was obtained, the heaters were turned on and the solutions
were allowed to come to an equilibrium reflux temperature. Then
BPO initiator was added to the reactor and a clock was started simul-
taneously. After an induction period of 3-5 min, the reactor temperature
elevation started dropping indicating that polymerization was occurring.
(Temperature elevation is an indication of monomer concentration as
explained in Section 5.0.) Additional samples were taken at approximately
uniform increments of temperature drop. The samples were inhibited
and stored in the manner previously described. The temperature
histories of both vessels were recorded and several atmospheric
readings were obtained. During the day following an experiment,
all of the samples were analyzed for monomer content using a
quantitative GC technique (see appendix).

Two experiments were conducted. In the first experiment
(C-5) 35 mole percent of the monomer was NFPA and sixty-five
percent was AA. In the second experiment (C-6), the percentages
were reversed. Monomer concentration histories for experiment C-5
are presented in Fig. 2. Similar results for experiment C-6 are given
in Fig. 3. Hand-smoothed curves are shown on the figures which are
felt to be most representative of the data. In drawing the smoothed
curves, an induction period equal to the time interval before the reactor
temperature started to drop was assumed. The initial monomer con-
centrations obtained from the initial batch weights were slightly
different from the initial concentrations obtained using GC analysis.
The average value from the two techniques was used in drawing
the initial conditions for the smoothed curves shown on the
figures.

The discrepancy in the initial monomer concentrations could
be attributed to several factors. The most probable cause of the
difference is believed to be error in the GC analysis due to a lack
of adequate temperature control on the GC oven. Other likely causes
are that the monomers may have been slightly impure or partially
polymerized or that a small amount of polymerization occurred during
storage before the samples were analyzed. Primary emphasis
in this report is given to the curves drawn through the average of the
initial concentrations from batch-weight and GC determinations as
shown in Figs. 2 and 3. However, the data were also reduced using
curves (not shown) drawn through initial batch weights as well as curves
drawn through initial GC data points. The copolymer reactivity ratios
and other results obtained using these two secondary techniques did
not differ greatly, and the results when averaged were the same as those
obtained using the primary data treatment.

3.0   REACTIVITY RATIOS

The composition of a copolymer formed by a free-radical
polymerization is generally considered to be governed by the copolymer
differential equation

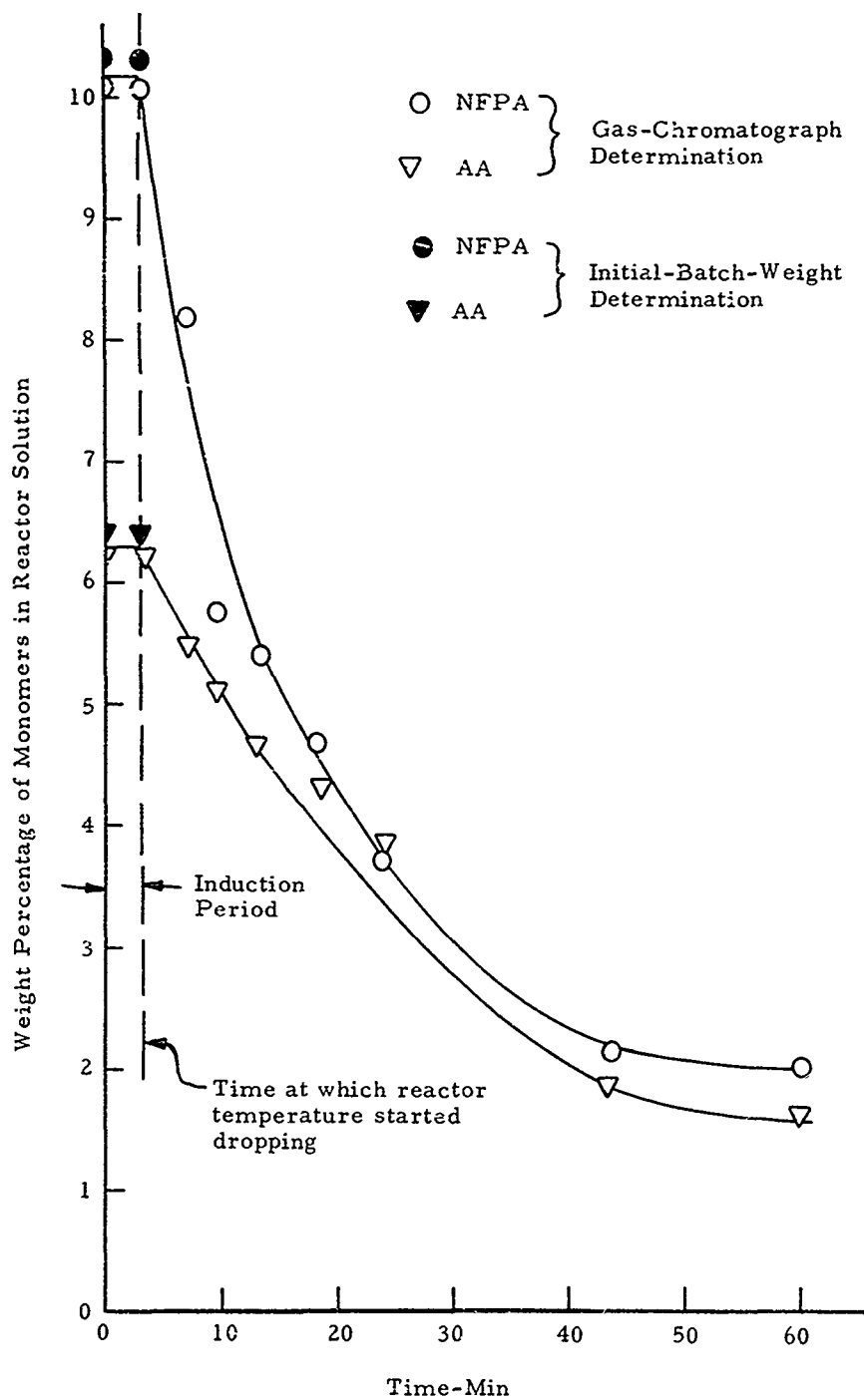$$\frac{d[M]}{d[N]} = \frac{[M]}{[N]} \frac{r_1[M] + [N]}{[M] + r_2[N]} \quad . \tag{1}$$

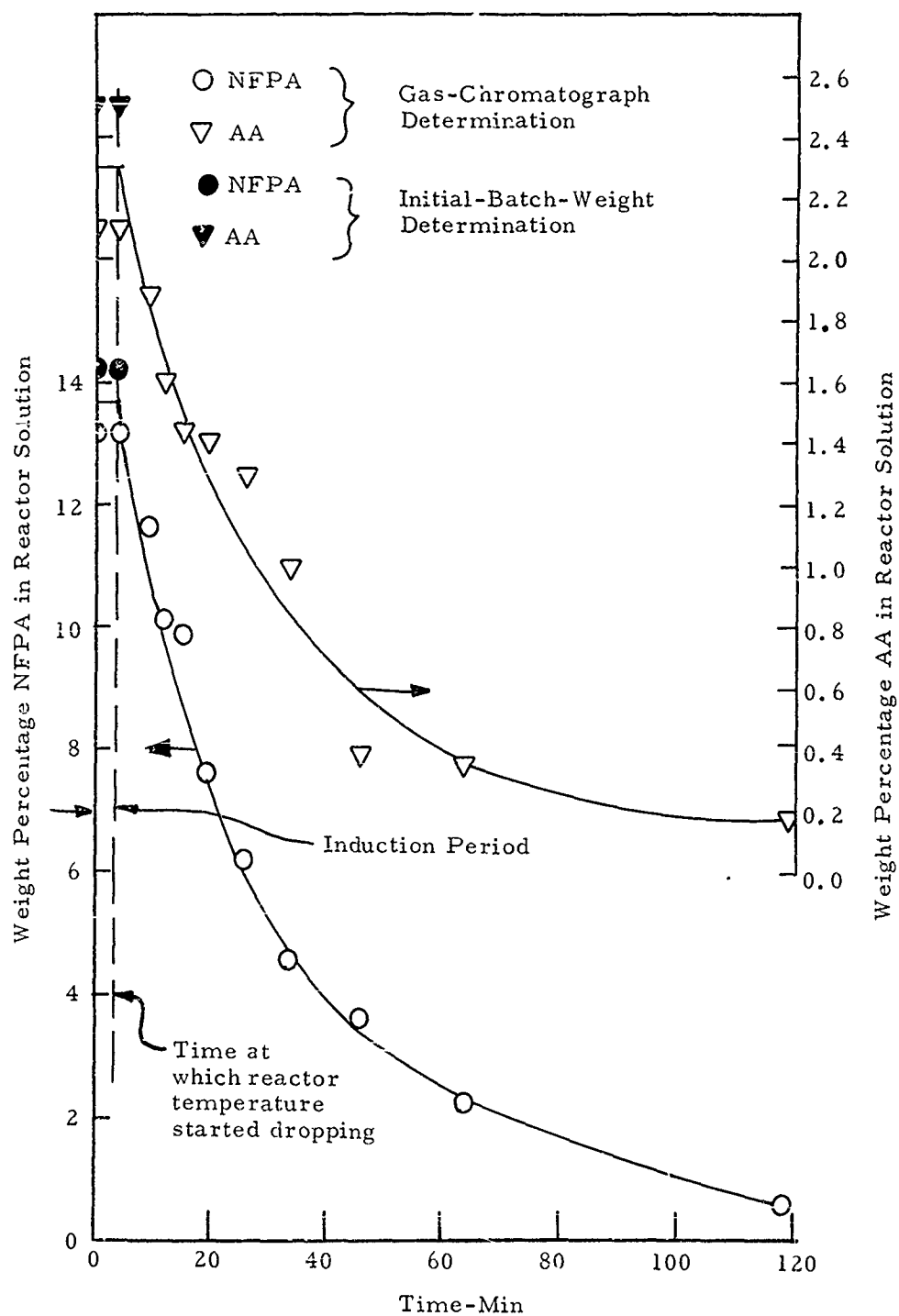Fig. 2 Monomer-Concentration History During Polymerization
Experiment C-5

Fig. 3 Monomer-Concentration History During Polymerization Experiment
C-6

In this case, [M] represents the concentration of AA in the solution, [N] represents the concentration of NFPA, and r_1 and r_2 are constants called reactivity ratios which must be determined experimentally. A derivation of the copolymer equations and a discussion on reactivity ratios can be found in standard texts on polymer chemistry [e.g., 4, 5]. Copolymer reactivity ratios are usually determined from a finite-difference approximation of the copolymer differential equation. This technique is easy to apply, requiring only the initial slope of a curve of [M] versus [N] for several experiments with differing initial concentrations. Unfortunately, the slope determined from curves of this type is always subject to more error than the curve itself. It was felt that a curve-fitting technique which fits the integrated copolymer differential equation to experimental data would be more accurate than the standard technique. In addition, the integral technique can utilize data obtained throughout a reaction rather than just those obtained at low conversions. Therefore, reactivity ratios derived from an integral curve-fitting technique should be more accurate and representative of the entire process.

The monomer concentrations can be normalized by use of the relations

$$C_M = [M]/\beta \quad \text{and} \quad C_N = [N]/\beta \quad ,$$

where β represents the total concentration of monomer in the total batch charge. Initially $C_M + C_N = 1$ for a batch process. Eq. 1 can then be normalized as

$$\frac{dC_M}{dC_N} = \frac{C_M}{C_N} \cdot \frac{r_1 C_M + C_N}{C_M + r_2 C_N} \quad , \tag{2}$$

a form more convenient to use for curve-fitting purposes when several experiments are utilized. The conversion or polymer fraction P can be obtained from the normalized monomer concentrations by use of the relation $P = 1 - C_M - C_N$.

Normalized concentration versus conversion plots were obtained
from the smoothed curves shown in Figs. 2 and 3 as shown in Figs.
4 and 5. The data points shown on these figures were obtained by
reading values from the smoothed curves of Figs. 2 and 3 at time
intervals corresponding to approximately uniform increments of
temperature drop (therefore, at approximate uniform increments of
monomer conversion). These data points were the ones used in the
integral-curve-fitting scheme which operated as follows. A pair
of values for r_1 and r_2 is assumed, the copolymer equation is integrated
numerically on a digital computer using the initial concentrations
for the experiment, and the results are stored in the computer at
convenient increments of conversion. Then by interpolation, using a
parabolic fit to three stored results in the neighborhood of each data
point, the difference (P calculated - P experimental) is determined
for each reduced monomer concentration data point in the experiment, e.g. data
points on Fig. 4. Finally, the standard deviation of these differences is calculated.
The standard deviation can be based on data from either one or both monomer con-
centrations. Data from more than one experiment can be utilized to determine a
single value of the standard deviation; of course, this requires a numerical
integration for each experiment from its initial condition. The above
procedure is followed for points throughout the region of interest in the
r_1, r_2 plane. Then a contour map containing lines of constant standard
deviation is plotted on a graph representing the r_1, r_2 plane. The entire
procedure was automated including the plotting of the graph; a minimum
of labor is required. Although a tremendous amount of computation is
required, the IBM 7094 computer time requirements are modest—
approximately 5 min per experiment.[1]

A contour map of the standard deviation in polymer fraction
(conversion) based on both monomers and both experiments is shown
in Fig. 6. The minimum standard deviation occurs at the point
$r_1 = 0.42$, $r_2 = 0.75$, and these values are considered to be the best

---

[1] A more complete description of the reactivity-ratio-determination
procedure including a listing of the FORTRAN computer program
and other programs mentioned in the report can be obtained from
the writer.

These solid lines were calculated from
the initial conditions using $r_1 = 0.42$,
$r_2 = 0.75$
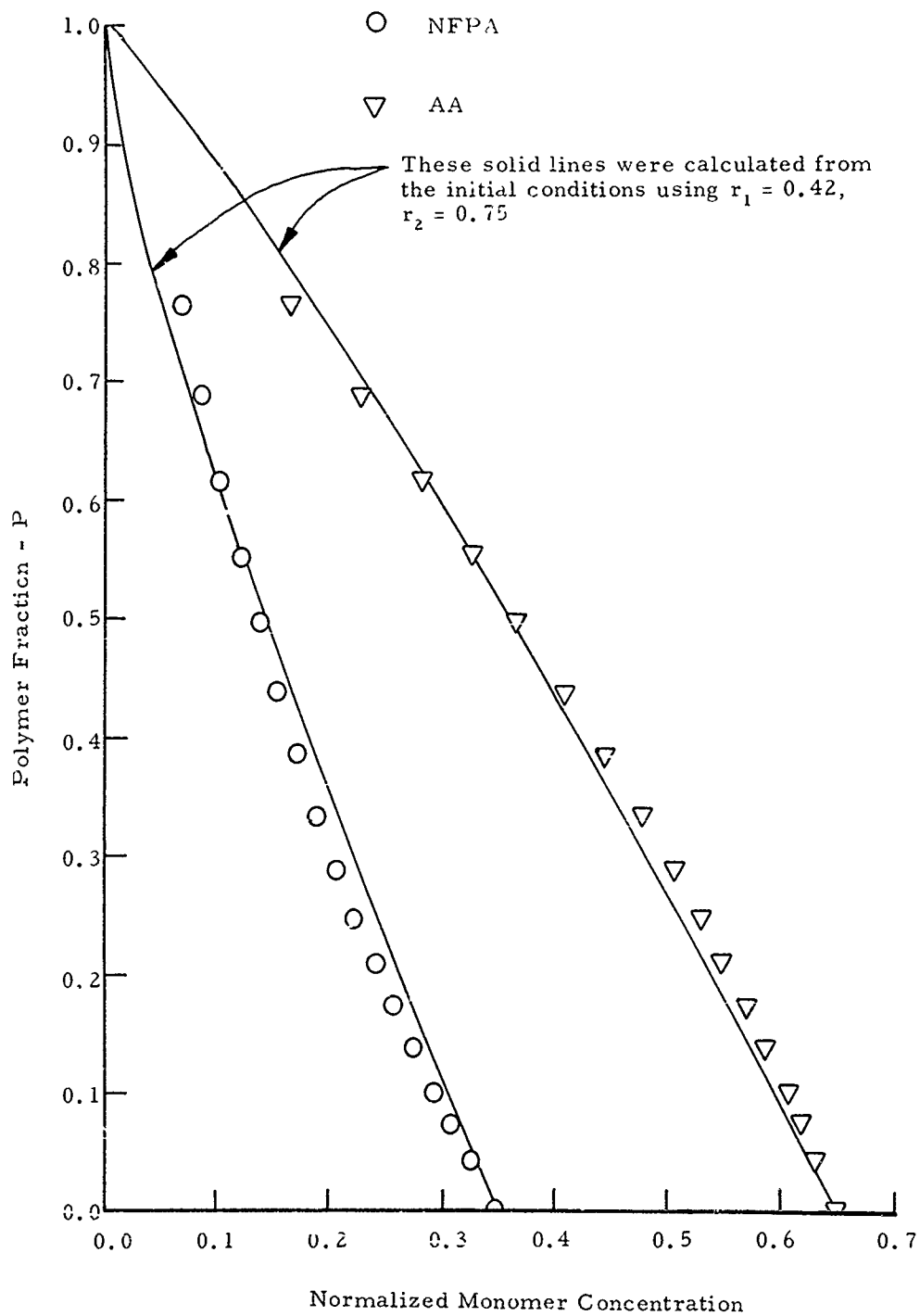
Fig. 4 Normalized Concentration-Conversion Plot, Experiment C-5
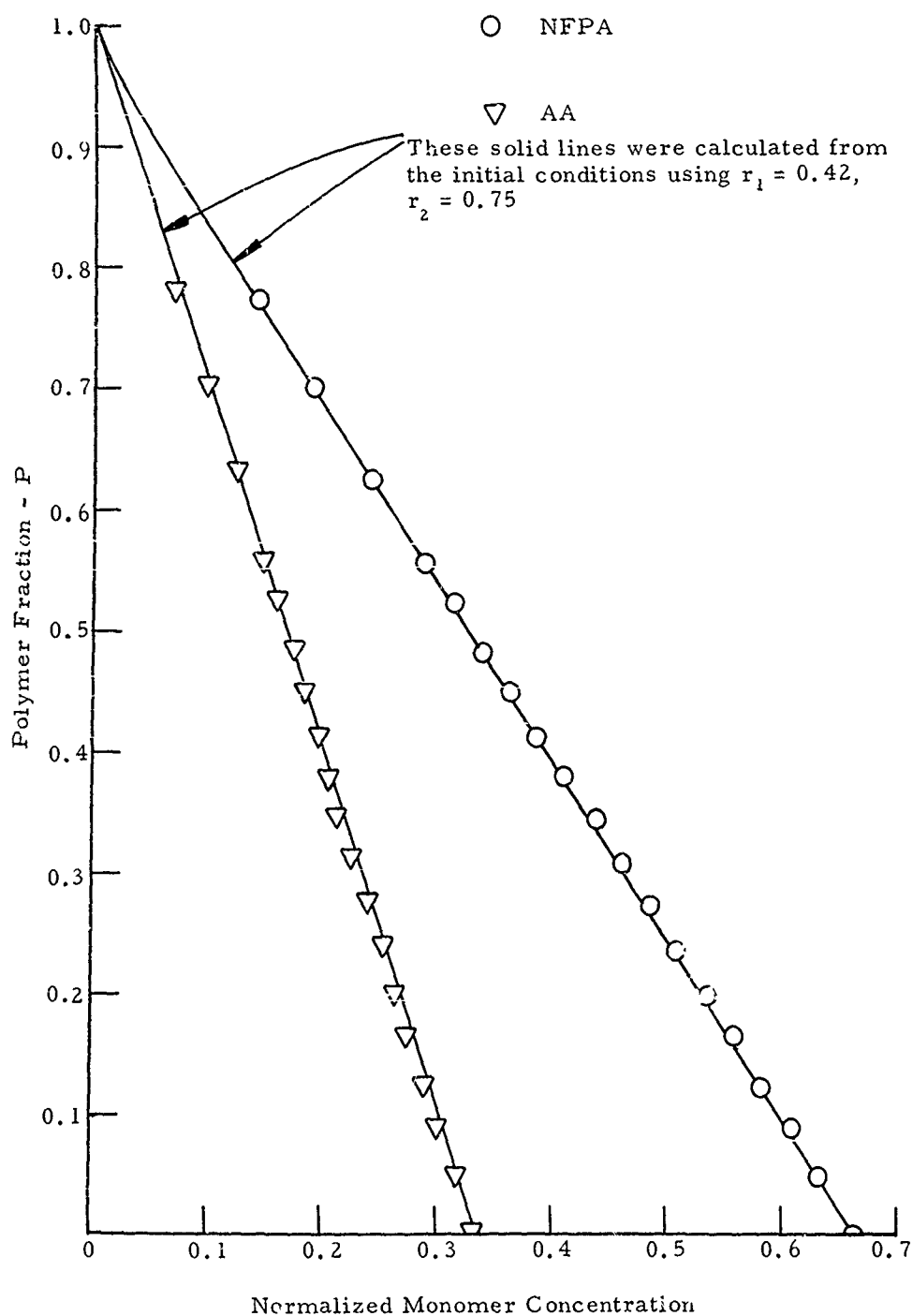
Fig. 5 Normalized Concentration-Conversion Plot, Experiment C-6

$$r_1 = 0.42 \atop r_2 = 0.75 \rbrace \quad \text{Approximate Minimum}$$
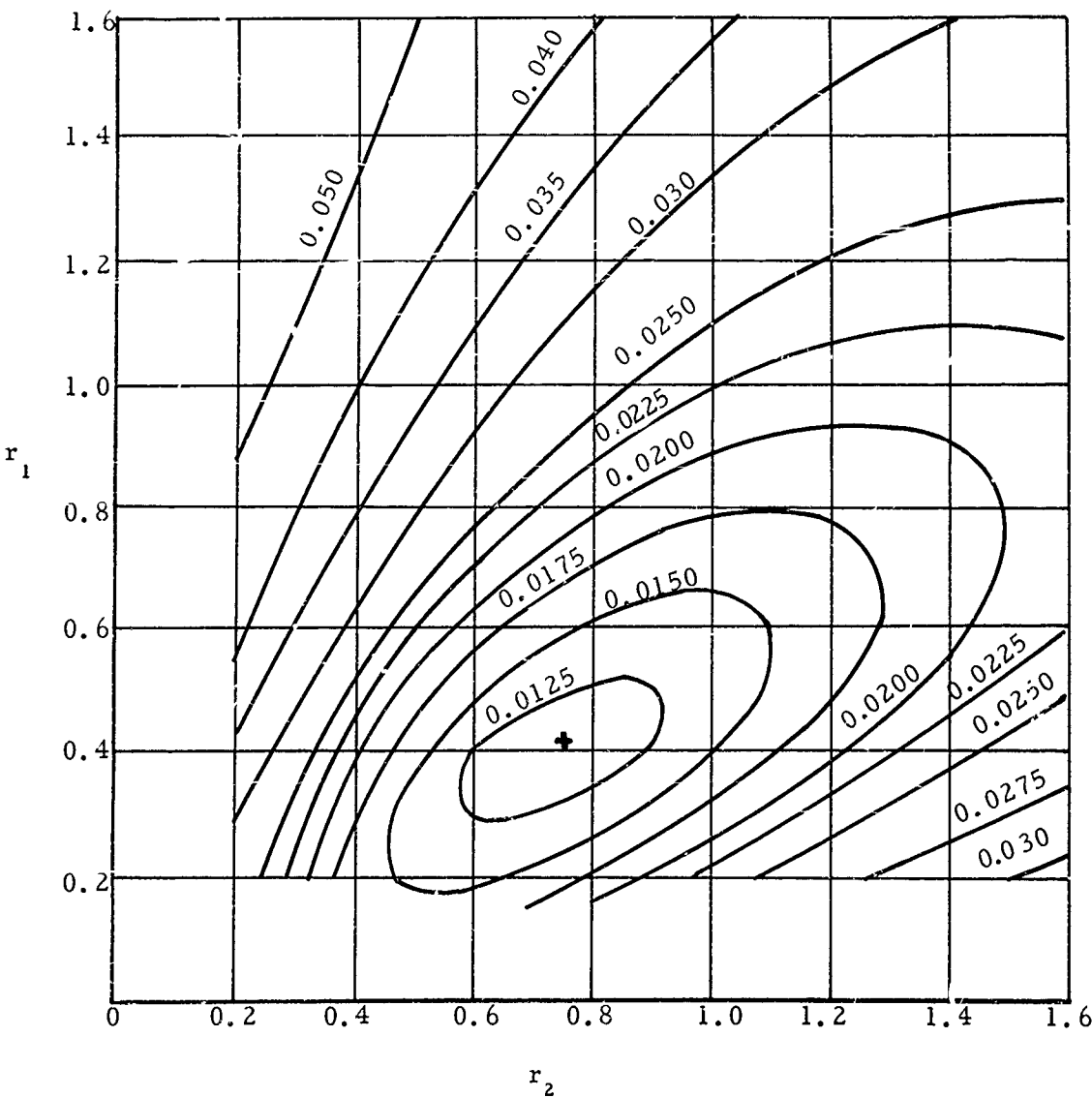

Fig. 6 Contour Map of Standard Deviation in r_1 , r_2 Plane

estimate of the copolymer reactivity ratios. When a similar data-
reduction procedure was employed using smoothed monomer-concentration
histories drawn through initial concentrations obtained from the initial
batch weights, the reactivity ratios obtained were $r_1 = 0.40$ and $r_2 = 0.60$.
Similarly, when the initial GC analysis data were employed, the
reactivity ratios were found to be $r_1 = 0.44$ and $r_2 = 0.90$. The average
of the results obtained from these two extreme initial-data treatments
are $r_1 = 0.42$ and $r_2 = 0.75$, the same as that obtained using the average
initial conditions as described above. It is felt that the differences in
these values serve as an indication of the magnitude of errors
resulting from inaccurate concentration measurements. The solid
lines in Figs. 4 and 5 were calculated using the best estimate of the
reactivity ratios, and the calculations are in good agreement with
the data.

4.0 POLYMER COMPOSITION

The reactivity ratios obtained from Fig. 6 are both less than
unity, indicating that there exists an azeotropic initial mole ratio
of monomers which will produce a perfectly uniform polymer with
respect to monomer composition. This composition is found by setting
the left hand side of Eq. 2 equal to the ratio C_{M_0}/C_{N_0} and solving
the resulting algebraic equation simultaneously with the relation
$C_{M_0} + C_{N_0} = 1$, where the zero subscripts indicate initial concentrations.
For the reactivity ratio pair obtained using the average initial
concentration employed in this report $(r_1 = 0.42, \ r_2 = 0.75)$, the
azeotropic AA concentration is $C_{M_0} = 0.30$. Similarly, for the one
extreme conditions of $r_1 = 0.4$, $r_2 = 0.6$, the azeotropic concentration
is $C_{M_0} = 0.40$; for the second extreme condition of $r_1 = 0.44$,
$r_2 = 0.90$, the azeotropic concentration is $C_{M_0} = 0.152$. The co-
polymers of interest for propellant binder applications contain
low AA mole concentrations in the range of 15% (i.e., $C_M = 0.15$)
The composition conversion curve for a 96/4 NFPA/AA weight-
ratio copolymer (11.1 mole percent AA) is shown in Fig. 7. The
average composition is shown as a dotted line on the figure, and
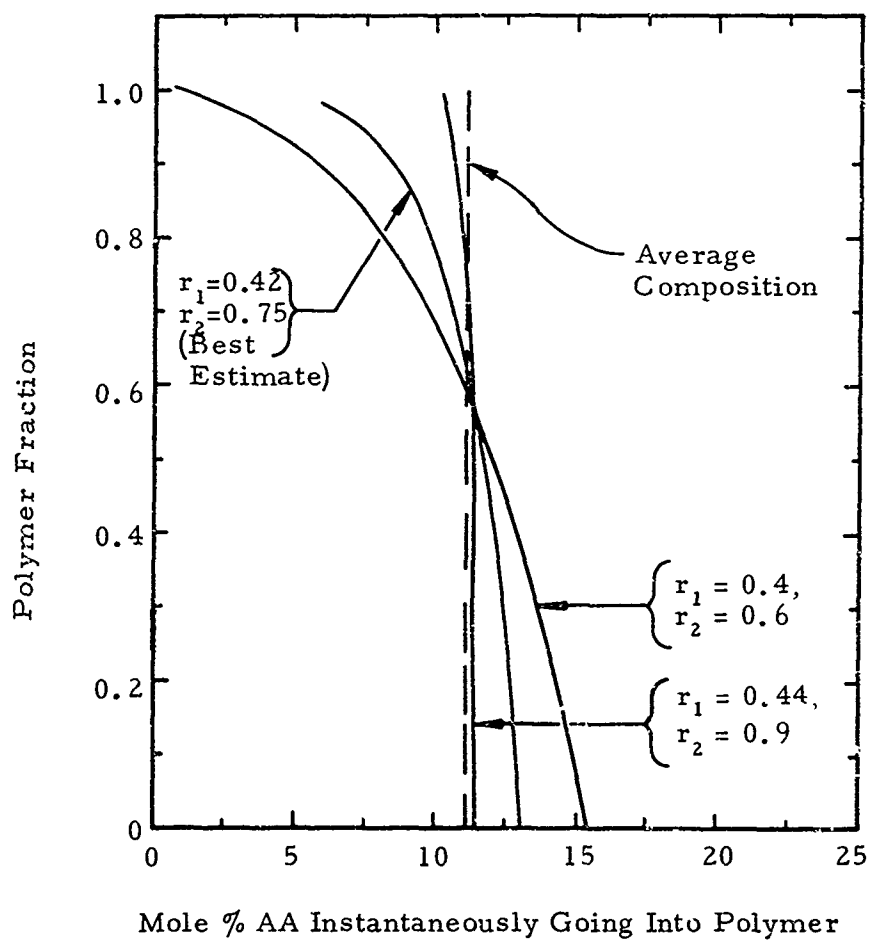
Fig. 7 Composition of Forming Polymer, 96/4 NFPA/AA Weight Ratio

composition conversion curves of all three reactivity-ratio pairs
which have been discussed are included. Similar results for a
94/6 copolymer are given in Fig. 8.

In an effort to confirm the reactivity ratios which were
obtained, an experiment run previously by the Polymer Chemistry
Group for a 94/6 NFPA/AA weight-ratio polymer was considered.
This experiment was carried out under reflux conditions at atmospheric
pressure in EtOAc solvent. The data were analyzed with a GC apparatus
using toluene as an internal standard. The toluene was added to the
solution just prior to the beginning of the experiment, and the samples
were analyzed immediately after they were taken to minimize problems
due to evaporation of the toluene. These data are shown in Fig. 9
along with curves calculated for the reactivity-ratio pair, $r_1 = 0.42$,
$r_2 = 0.75$. Partial results are also included for the other reactivity-
ratio pairs. The agreement between the calculations and the data
is excellent, although the calculated results for any of the reactivity
ratio pairs are not really greatly different.

An interesting observation can be made by examining Figs. 8
and 9. The normalized monomer concentration-conversion curves
of Fig. 9 are not very different whereas the instantaneous polymer
composition-conversion curves of Fig. 8 are considerably different.
Another means of confirming the reactivity-ratio results is to stop
the reaction before it has progressed very far, separate the polymer
that is formed, and compare the measured AA content of the polymer
with calculated results of the different reactivity-ratio pairs. Infrared-
absorption calibrations obtained by the Analytical Chemistry Group
indicate that the AA content of the copolymer can be determined to
within 10% of the AA level by weight. Calculations were made to
determine if suitable experimental conditions could be found which would
allow a distinction to be made between the reactivity-ratio estimates.
Fig. 10 shows a plot of the calculated normalized AA concentration
of the first bit of polymer formed versus the normalized AA content
in the reactor solution. Calculated curves are shown for the two
extreme pairs of reactivity ratios along with a curve indicating the
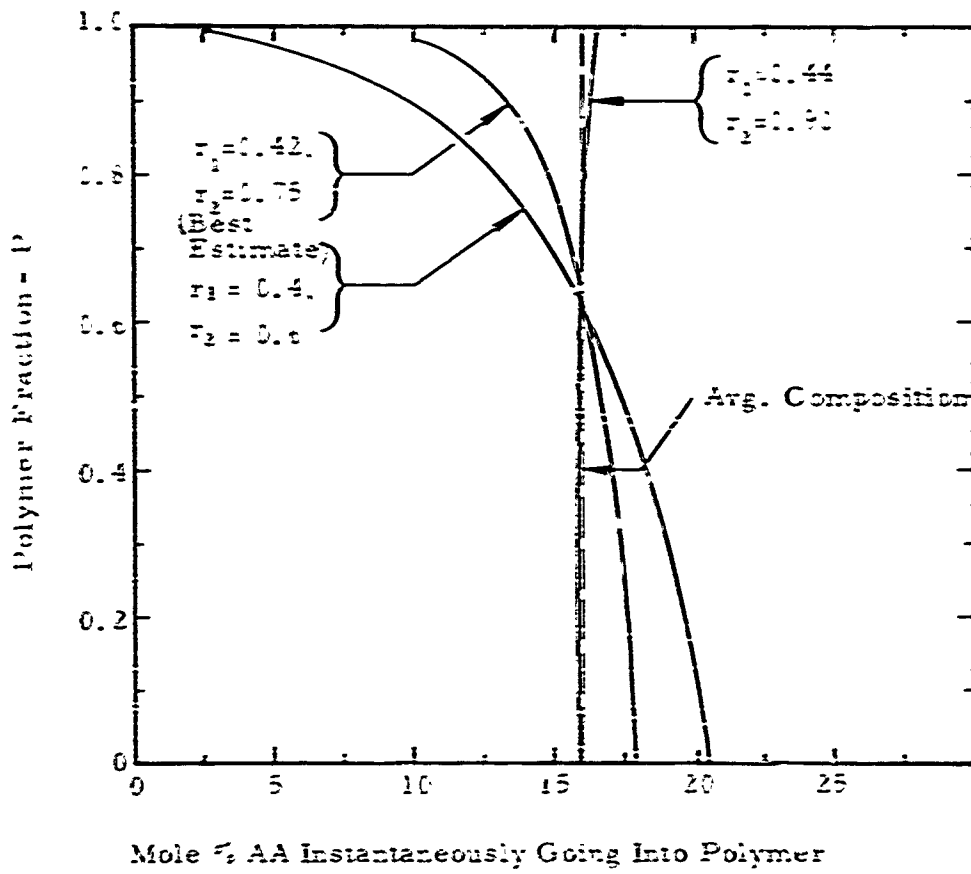
Fig. 8 Composition of Forming Polymer, 94, 6 NFPA/AA Weight Ratio
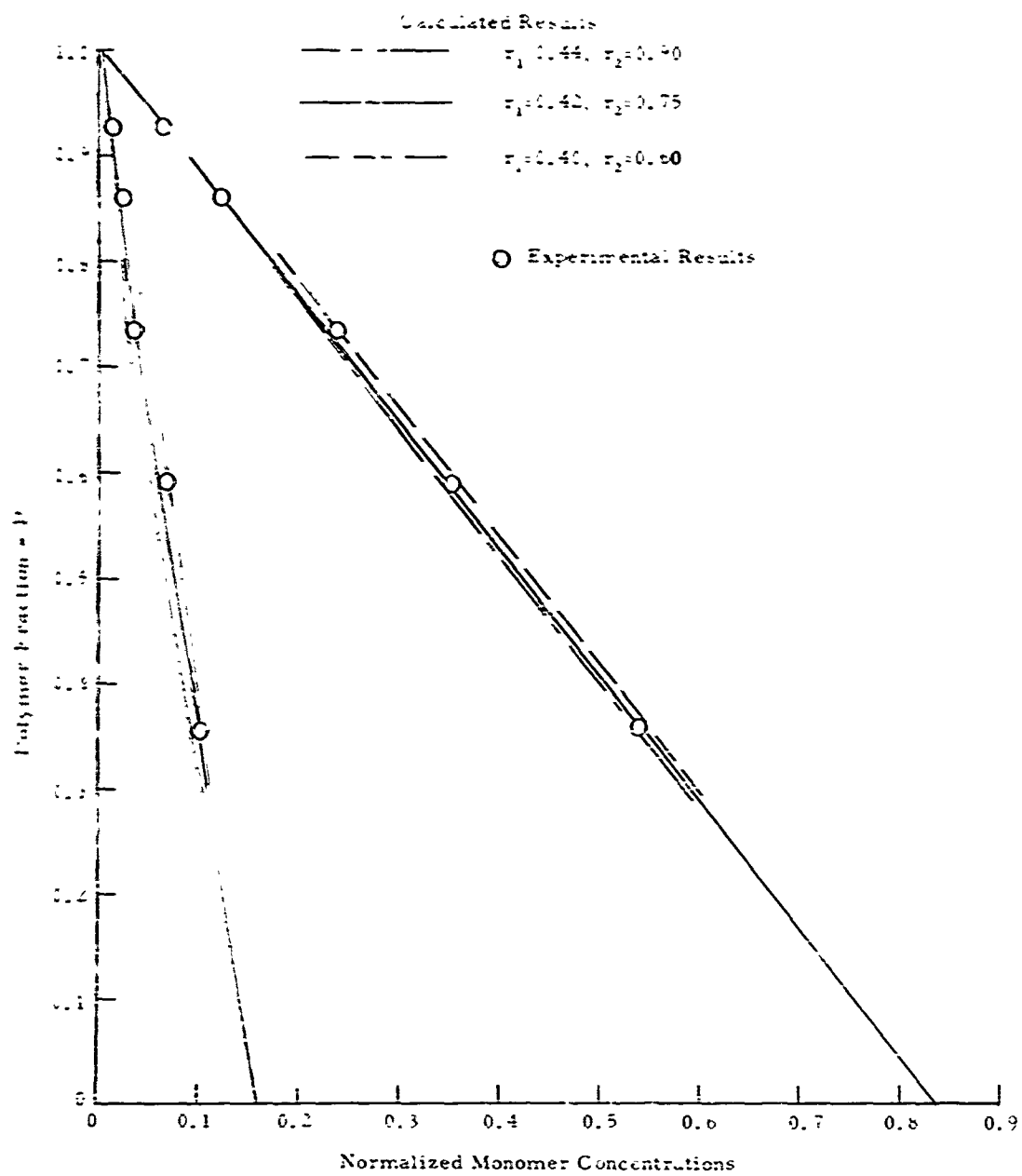
Fig. 2 Normalized Concentration-Conversion Plot, 94/6 NFPA/AA Weight-Ratio
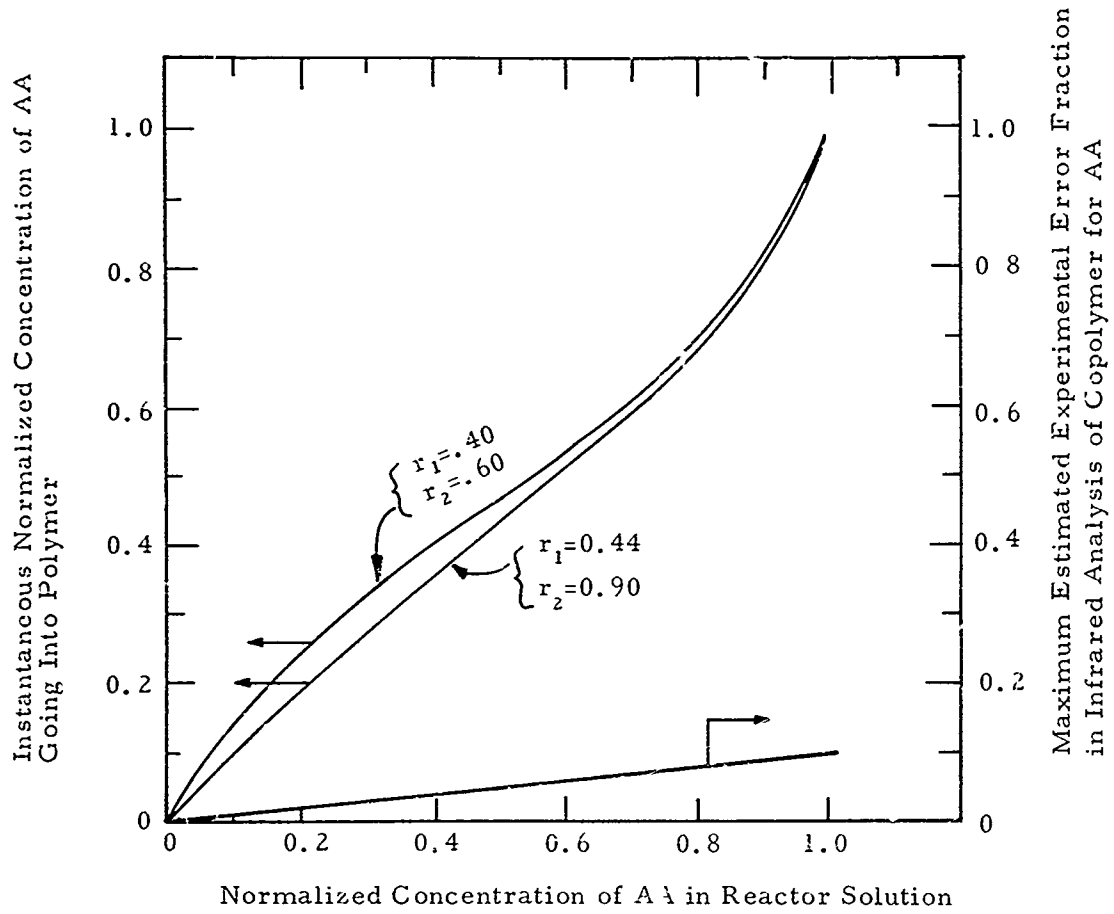Copolymer

Fig. 10 The Effect of Reactor Concentrations on Polymer Composition

magnitude of the uncertainty of the infrared absorption analysis
mentioned previously. For normalized AA concentrations in solution
of about 0.16, or less, the calculated difference in the composition
of the first amount of polymer formed for the two extremes in reactivity
ratio pairs is more than twice the uncertainty in the infrared analysis.
Therefore, it was felt that a distinction between reactivity ratios
could be made for an experiment conducted under these conditions and
accordingly a 94/6 weight ratio NFPA/AA copolymer batch process
was selected for this test, a process which initially has a reduced
solution concentration of AA of 0.161. The reaction was run to
approximately 20% conversion and stopped. The polymer was separated
and analyzed for AA content by infrared analysis. For the reactivity-
ratio pair, $r_1 = 0.42$, $r_2 = 0.75$, the calculated and experimental AA
concentrations for 20% conversion were very close—the experimental
value was 17.7 ± 1.8 (15.9 to 19.5) mole % AA and the calculated
AA concentration was 17.6%. Use of $r_1 = 0.40$ and $r_2 = 0.60$ resulted
in a calculated composition for 20% conversion of 20.1 mole % AA
while use of $r_1 = 0.44$ and $r_2 = 0.90$ resulted in a composition of 16.0
mole % AA.

Based on all of the above data it is felt that the best estimates
for the copolymer reactivity ratios are $r_1 = 0.42$ and $r_2 = 0.75$. The
other combinations which have been discussed are felt to indicate
reasonable limits for the reactivity ratios.

Reactivity ratios are useful in calculating detailed statistical
information about a polymer chain as well as for predicting its average
composition. In a recent paper by Ito and Yamashita [6], copolymer
composition and microstructure were discussed. The copolymer differential
equation is based on a simple terminal process and if this is assumed,
the authors give the following expressions for the number-average
run lengths of monomer units in the forming polymer chain:
$\ell_M = 1 + r_1 X$, $\ell_N = 1 + r_2/X$, where ℓ_M is number-average run
length of AA units, ℓ_N is the number-average run lengths of NFPA
units, and X is the mole ratio C_M/C_N in the reactor at a given time.

From these expressions it is evident that for the copolymers under consideration, the number-average AA run length is never much greater than unity.

5.0 TEMPERATURE ELEVATION

Considerable effort was devoted to obtaining an accurate measurement of the temperature elevation of the actual reactor over a similar vessel containing only EtOAc. Consideration will now be given to the theoretical temperature elevation in relation to monomer concentration, and in a later section the temperature elevation will be used in polymerization-rate studies.

The vapor pressure of a pure vapor in equilibrium with its liquid phase is usually found experimentally to obey a relation of the type

$$\ln P_{v_i} = A - \frac{B}{T} \quad , \tag{3}$$

where P_{v_i} is the vapor pressure, T is the absolute temperature, and A and B are constants. When a vapor is in thermal equilibrium with an ideal mixture of liquids, the partial pressure of a component in the vapor phase is ideally represented by

$$P_i = X_i P_{v_i} \quad , \tag{4}$$

where P_i is the partial pressure of the ith vapor component, X_i is the mole fraction of the ith component in the liquid phase, and P_{v_i} is the vapor pressure that would exist at the mixture temperature if a pure liquid phase of the ith component were present.

Each reactor was constructed so that it could operate at atmospheric pressure. The vapors were condensed and returned to the vessel and the vapor volume was small enough that the mass in the vapor phase could be neglected. Moisture was prevented

from entering the reactor by the use of a Drierite® [*] column for the vent to the atmosphere. In this reactor, the total pressure of a well-stirred, boiling ideal solution is atmospheric P_T and equal to the sum of the partial pressures of the components in the reactor. That is,

$$P_T = \sum_i X_i P_i (T) .$$

(5)

The boiling temperature of such a mixture is that temperature necessary to establish the pressure equilibrium indicated in Eq. 5. Each component i contributing to the pressure has a vapor pressure-temperature relationship of the type given in Eq. 3. Thus Eq. 5 can be written as

$$P_T = \sum_i X_i e^{A_i - B_i/T} .$$

(6)

Eq. 6 can be solved by an iterative technique to obtain the mixture boiling temperature T. Newton's method has proved to be a convenient iterative technique for computer use.

Polymer molecules make a negligible contribution to the pressure and mixture mole fractions due to the very large molecular weight of the polymer. Therefore, the important components in Eq. 6 are the solvent and the comonomers. The initiator also makes a minor contribution to the mole fraction, but exerts no appreciable pressure since it is a dissolved solid. Vapor pressure data for the EtOAc solvent and the AA monomer were obtained from a standard reference [7], but the NFPA vapor pressure was measured [8]. These data are shown graphically in Fig. 11. Calculations were made of the reactor temperature elevation as a function of conversion for experiments C-5 and C-6. These calculated curves are shown with the corresponding experimental data in Fig. 12. For these calculations, the reactivity ratios were assumed to be $r_1 = 0.42$ and $r_2 = 0.75$. However the temperature elevation calculations proved to be very insensitive to reactivity ratios. The agreement between the theoretical and experimental temperature elevation is satisfactory.

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[*] Trademark of W. A. Hammond Drierite Co., 122 Dayton Ave., Xenia, Ohio.
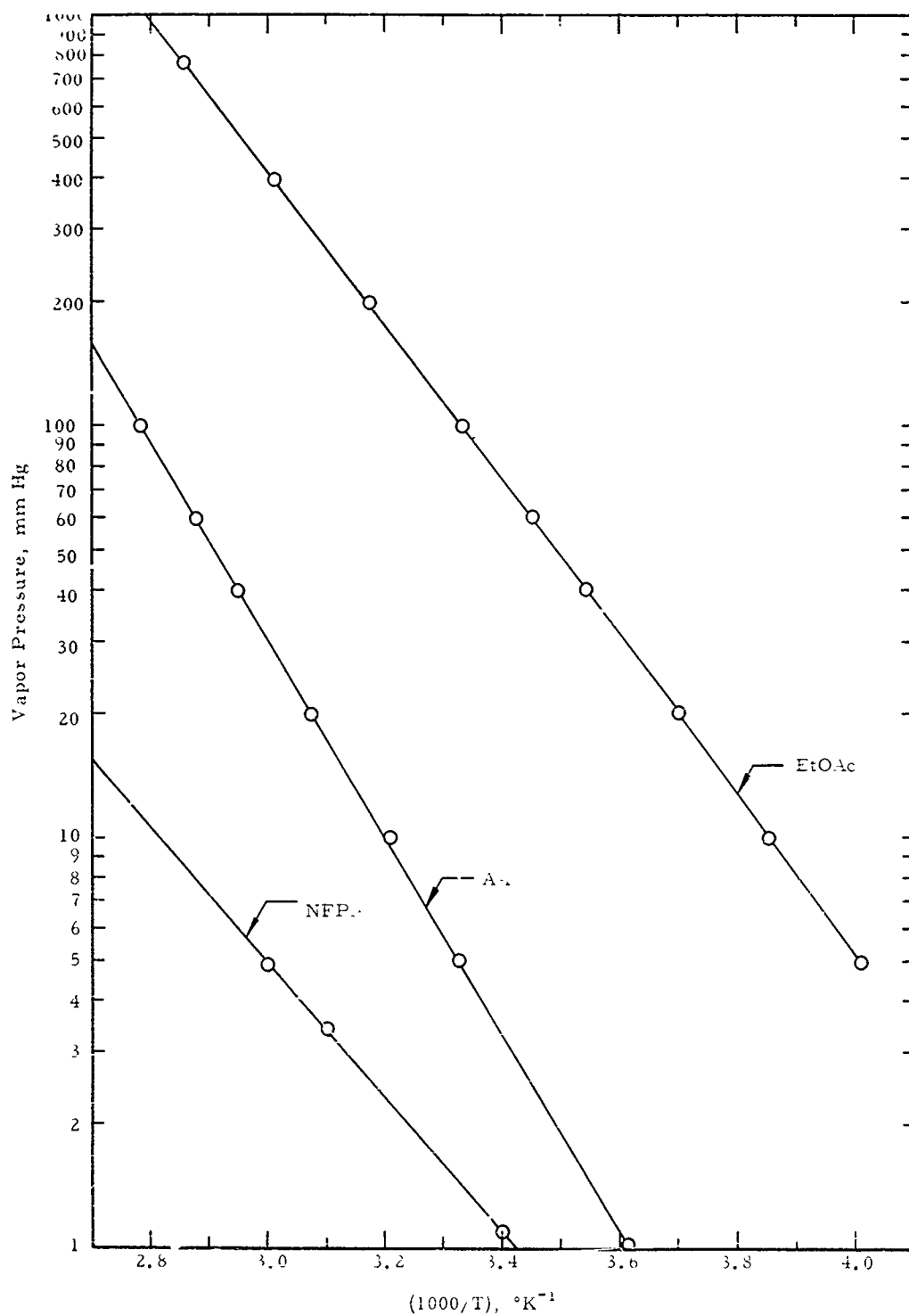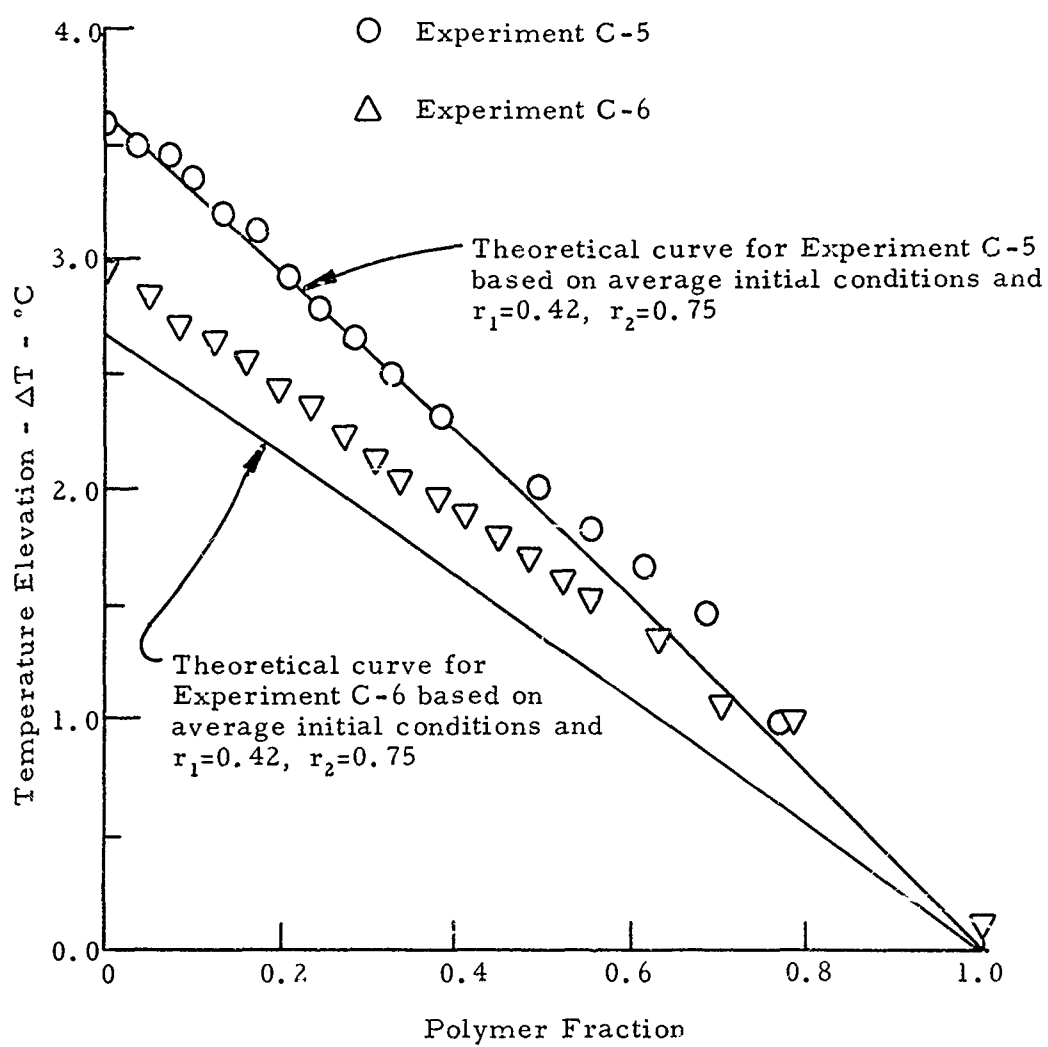
Fig. 11 Vapor Pressure of Reactor Components

Fig. 12 Temperature Elevation vs. Conversion

6.0 POLYMERIZATION RATE

A sufficiently accurate mathematical model of the polymeriza-
tion rate can be of considerable value in process development. Since
the copolymers of interest in this report are composed largely of NFPA,
with the AA content being 15 mole percent or less, the simplest choice
for a rate model is to assume that the copolymerization can be treated
as a homopolymerization. This choice is more logical for copolymers
which form a reasonably uniform product such as NFPA and AA
apparently do. The kinetics of free-radical-induced homopolymerization
are described by the equation

$$\frac{d[\tilde{M}]}{dt} = -K[\tilde{M}][I]^{\frac{1}{2}} \quad , \tag{7}$$

where $[\tilde{M}]$ is the total monomer concentration, $[\tilde{M}] = [M] + [N]$,
$[I]$ is the initiator concentration, t is time, and K is the polymerization
rate constant.

A derivation of the rate expression given in Eq. 7 can be found
in standard texts [e.g., 4, 5]. One assumption made in the derivation
of Eq. 7 is that chain termination occurs from radical interaction
(either coupling or disproportionation). A kinetically similar situation
exists when radical chain transfer occurs with the solvent. The chain
transfer step is one in which a growing chain is terminated by abstracting
a radial fragment from a solvent molecule. The remaining solvent
molecule fragment then initiates a new polymer chain and in effect does
not influence the overall polymerization rate. Chain transfer, however,
does exert a large influence on polymer molecular weight. A discussion
of the effect of chain transfer on polymer molecular weight is given
in Section 7. It is believed that chain transfer is the dominant mode
of chain-growth termination in the processes under consideration in
this report, and some justification of this belief is given in Section 7.

6.1 Initiator Decay Rate

Considerable work on the decomposition of BPO initiator has
been reported in the literature and much of this work is summarized

by Tobolsky and Mesrobian [9]. The spontaneous decomposition rate of BPO has been found to depend on the solvent. For EtOAc solvent, the decomposition rate of BPO is correlated by the equation

$$\frac{d[I]}{dt} = -k_d [I] , \qquad (8)$$

where [I] is the initiator concentration in $\frac{\text{moles BPO}}{\text{liter of solution}}$ and

$$k_d = 1.51 \times 10^{16} \exp \frac{-15,000}{T_{abs} \, ^\circ K} / \text{min.} \qquad (9)$$

If a large radical concentration is present, radical-induced decomposition of the BPO may also occur. For very large concentrations of BPO in EtOAc solvent, radical-induced decomposition has been found to increase the decomposition rate by a factor of 5. However, if the BPO concentration is low and monomer molecules are present, the radicals tend to attack the monomer molecules in preference to BPO. Therefore, for the polymerization conditions used in this work it was felt that the initiator decomposition equations given above should prove suitable for use.

Nevertheless, some experimental verification of the decomposition rate was desired. Attempts to measure the BPO concentration in samples taken from the reactor as the reaction progressed were abandoned after several problems arose. (Presence of the NFPA molecule excludes from use most conventional quantitative analysis techniques for measuring BPO concentrations. In fact, the presence of NF_2 groups has been found to interfere with many conventional analytical techniques.) An indirect verification of the accuracy of the decomposition rate was provided by some preliminary experimental work on an incremental-addition copolymerization process. In this preliminary experiment, EtOAc solvent, BPO initiator, and a mixture of butyl acrylate and AA monomers were placed in the reactor and heated to the reflux temperature. The temperature elevation was measured by the

technique described earlier. When the temperature elevation had dropped by 40%, an additional charge of the monomer mixture was added to bring the temperature elevation (and therefore the monomer concentration) back to the original value. This addition procedure was repeated four times. The polymer that was formed exerted only a small influence on the monomer and initiator concentrations by a dilution effect. Therefore, the major change in the polymerization rate from one addition to the next should come from a reduced initiator concentration due to initiator decay. If the initiator-decay rate constant given in Eq. 9 is correct, the polymerization rate after the fourth addition should have been reduced from that of the original charge by about 30%. Fig. 13 shows the temperature elevation as a function of time after each addition for this experiment. From this figure it can be seen that the response time of the first addition was about the same as for the original charge and that the response time of the fourth addition was increased by the appropriate amount (about 40%). Therefore the initiator-decomposition rate constant given in Eq. 9 was assumed to be satisfactory.

6.2 Polymerization-Rate Correlation

Polymerization-rate data were obtained by three different means. One te' ique used was to follow the monomer-concentration histories in a reactor by analyzing samples taken from the reactor using GC techniques. A second technique was to follow the temperature elevation in a reactor operating under reflux conditions. Both of these techniques have been discussed above. A third technique was to follow the shrinkage of a sample in a dilatometer which is immersed in an isothermal bath. When the third technique is used, conditions which produce high polymerization rates must be avoided or a nonisothermal condition will exist. The dilatometric-shrinkage-rate data included in this report were for conditions which produced low reaction rates and negligible exotherms in the dilatometer. Other data have been obtained and reported in the past by others which did not always meet this condition. Temperature exotherms in dilatometers were measured for several conditions to establish that the data included in this report were reliable.
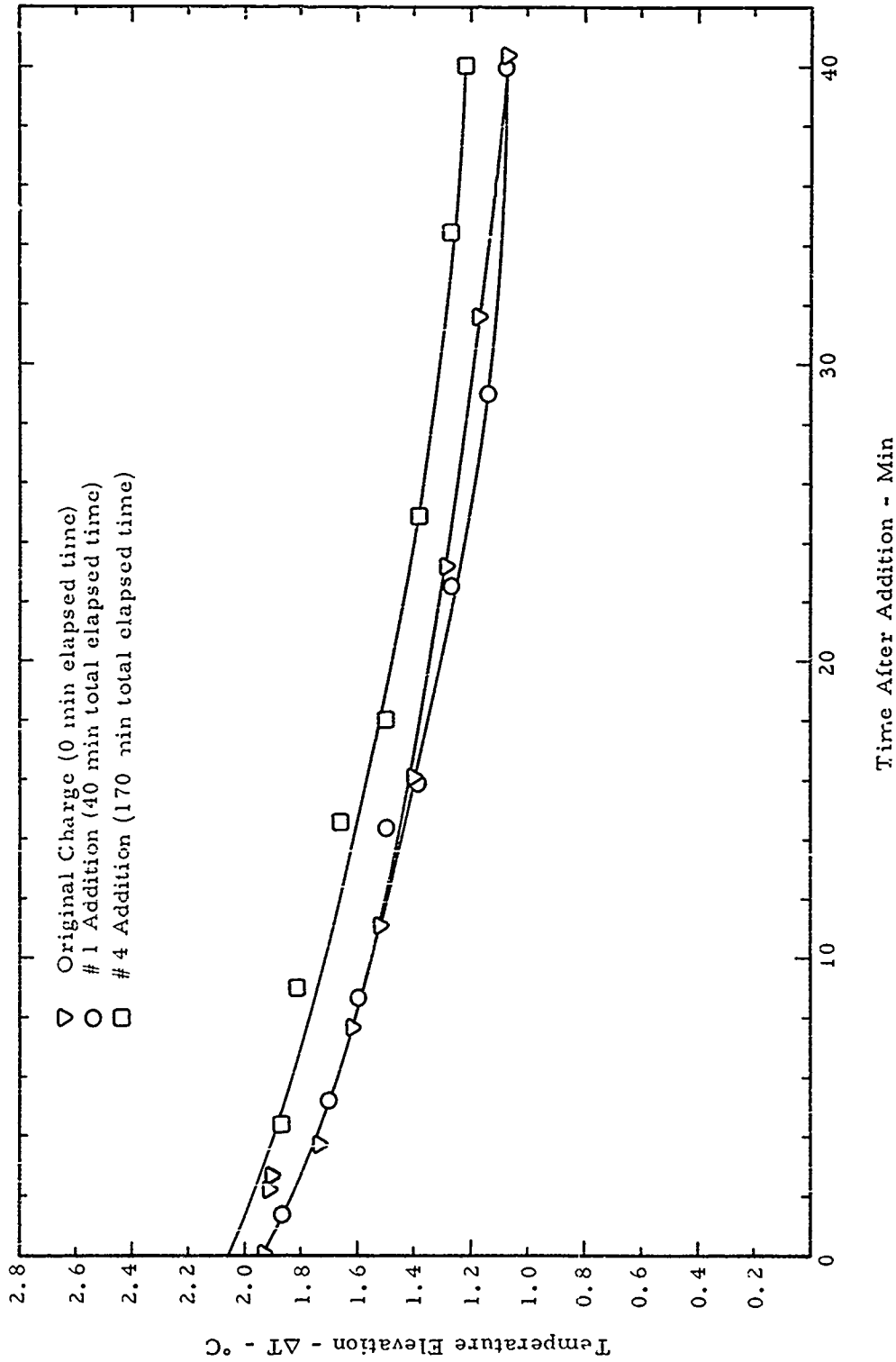
Fig. 13 Preliminary-Addition-Process Experiment with Butyl Acrylate and AA Monomers

All of the acceptable polymerization-rate data that was obtained involving mixtures of NFPA and AA monomers and BPO initiator were successfully correlated by a single polymerization-rate model. The procedure used to obtain the final model was tortuous and indirect. The rate model indicated in Eq. 7 was found to be inadequate in some of the early experiments. Several new models were hypothesized and those which could be made to fit the available data were tested with additional experiments which were designed to test their validity. Finally a model was found which correlated all of the data satisfactorily.

In fitting constants to the polymerization-rate model, no effort was made to include the rate data obtained in the reactivity-ratio experiments (described above) which contained high AA contents. Efforts were restricted to experiments in which the monomer charge was 94 or more weight percent NFPA. However, after the final correlation was obtained, the model was found to represent the high-acrylic-acid-content data as well.

The final rate model chosen included the initiator decay rate given previously in Eqs. 8 and 9. The polymerization rate model given in Eq. 7 was modified to the following form,

$$\frac{d[\tilde{M}]}{dt} = K f [M] [I]^{\frac{1}{2}} \quad . \tag{10}$$

The rate constant K was described by the Arrhenious-type relation

$$K = 1.8 \times 10^{16} \exp\left(\frac{-15,000}{T_{abs}{}^\circ K}\right) \frac{(\text{moles BPO}/\ell)^{-\frac{1}{2}}}{\text{min}} \quad . \tag{11}$$

The factor f was included to account for the observed decrease in the rate constant as the polymer concentration in the solution increased The equation describing f was found to be

$$f = e^{-0.8Q} \quad , \tag{12}$$

where Q represents the moles of monomers incorporated in polymer
per liter of solution. It should be emphasized that several rate
experiments with different initial values of Q were included in the
results and that, of course, Q increases as a reaction progresses
even if there is no initial polymer present.

A digital computer program was written for the rate model
described by Eqs. 8 to 12. The program has the following features:
(1) A constant temperature may be specified or a reflux operation
at atmospheric pressure can be used in which the boiling temperature
is calculated as the reaction progresses. (2) Polymerization shrinkage
is accounted for in the concentrations based on ideal solution behavior
of the components. (3) The assumption is made that the polymer pro-
duct which is formed has the same composition as the monomers
in the reaction solution. (Previous work described in the report
indicates that this assumption is approximately true. Also, it was found
that the reflux temperature is very strongly dependent on the total
monomer concentration and only very weakly dependent on the monomer
composition.) (4) The program is written in FORTRAN language
and employs an explicit-finite-difference technique to solve the differential
equations.

Since there is no one rate constant which can be easily obtained
and presented graphically to demonstrate the success of the correlation,
the experimental data is presented along with corresponding calculations
in Figs. 14-22. The differences between the calculated curves and the
data shown in these figures is due in part to experimental error, in part
to errors in the polymerization-rate model, and in part due to errors
in the temperature elevation model. In all cases the induction period
ends with the zero time shown on the figures. This includes all of
the available polymerization-rate data using BPO initiator which was
judged to be sufficiently accurate to use. In Fig. 14 the polymer
fraction history is presented for the data previously shown in Fig. 9
in conjunction with the reactivity-ratio work. Figs. 15 and 16 give
the temperature-elevation histories of the two experiments which were
used in the reactivity-ratio determination and previously discussed
in Section 3.0. The data obtained from an early attempt to utilize

a small-scale addition process is shown in Fig. 17. In this experiment
a new charge of monomer was added each time the temperature dropped
a predetermined amount. The monomer was added remotely from a
graduated burette by operating an air valve which in turn actuated a
pinch clamp on a rubber hose connecting the burette to the reactor.
The monomer level in the burette was monitored on closed-circuit
television. The quantity of monomer added in each charge may not
have been exactly the amount desired due to experimental difficulties.
A fourth addition was made but the material becomes too viscous for
the magentic stirrer to operate properly and no meaningful tempera-
ture measurements were obtained for this addition. In Fig. 18
data from two experiments are shown which was obtained for a 95/5
NFPA/AA monomer weight ratio with no initial polymer. Figs. 19
and 20 present data obtained under similar conditions where polymer
was added to the original mixture. The monomer concentration history
obtained from dilatometer shrinkage data at 75°C for NFPA monomer
is shown in Fig. 21, and similar results at 70°C are shown in Fig. 22.

The overall agreement between the calculated results and the
experimental data is considered excellent. The data were obtained
for a wide variety of experimental conditions which when considered
together severely test the rate model. The fact that excellent overall
agreement is demonstrated for such a wide variety of conditions lends
confidence to studies involving mathematical simulation of the process.

7.0 MOLECULAR-WEIGHT MODEL FOR CHAIN TRANSFER WITH SOLVENT

7.1 A Few Observations

As mentioned in Section 6, it is believed that for the system
under consideration, radical chain termination is primarily a result
of chain transfer with the solvent. While there is no absolute justi-
fication for this hypothesis, there is much qualitative supporting evidence,
some of which is given in the following paragraphs.

It has been experimentally observed that the molecular weight
of the copolymer product is relatively independent of initiator con-
centration over a very wide range of initiator concentrations. This

GC Experiment
5-min Induction Period
(Precharged Batch)

$[I_o] = 0.0063$ moles/ℓ
$[\tilde{M}_o] = 0.7726$ moles/ℓ

Batch Ingredients
14.71 gm NFPA
0.938 gm AA
83.9 gm EtOAc
0.161 gm BPO
0.0 gm Polymer
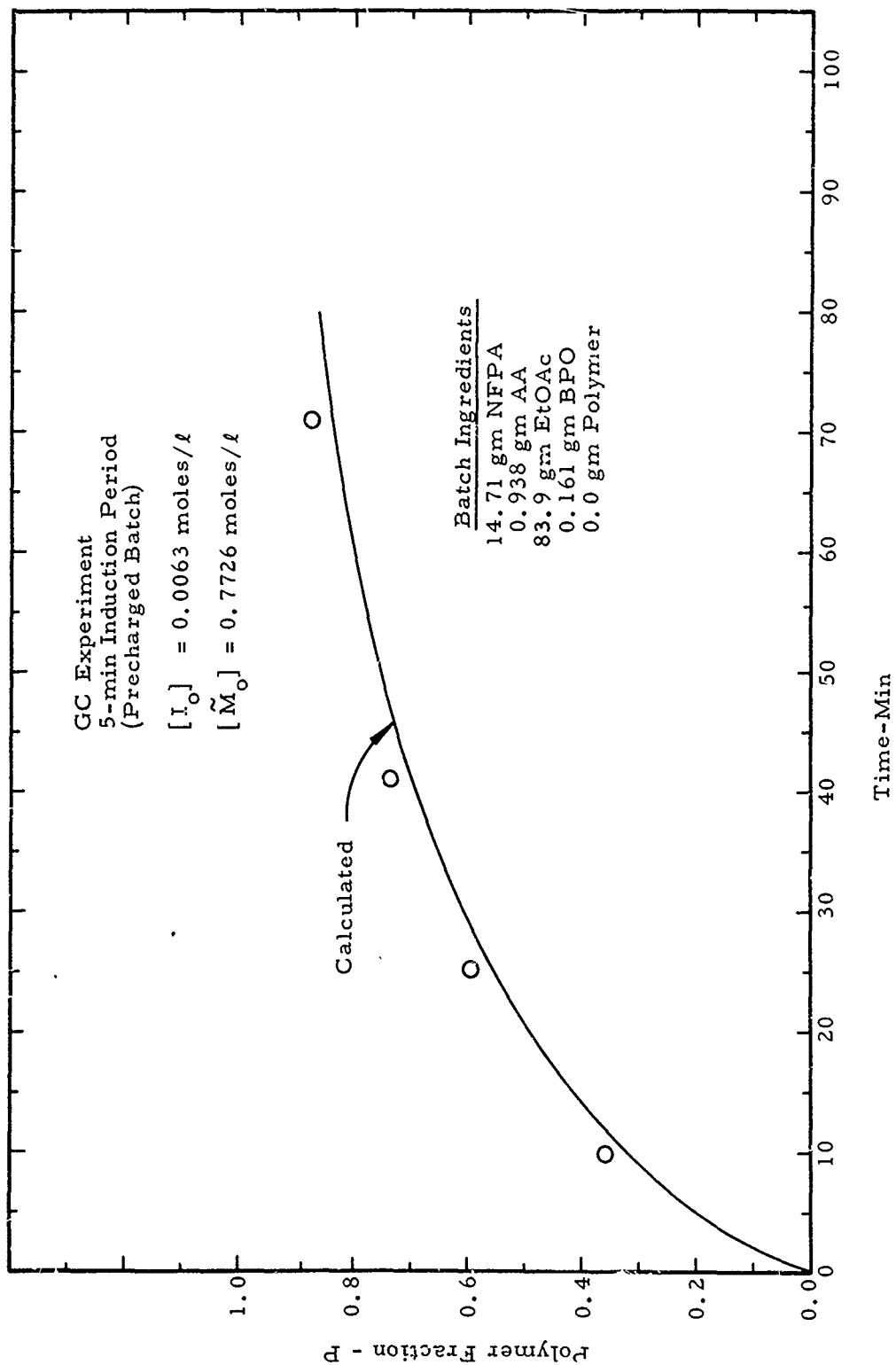
Calculated

Polymer Fraction - P

Time-Min

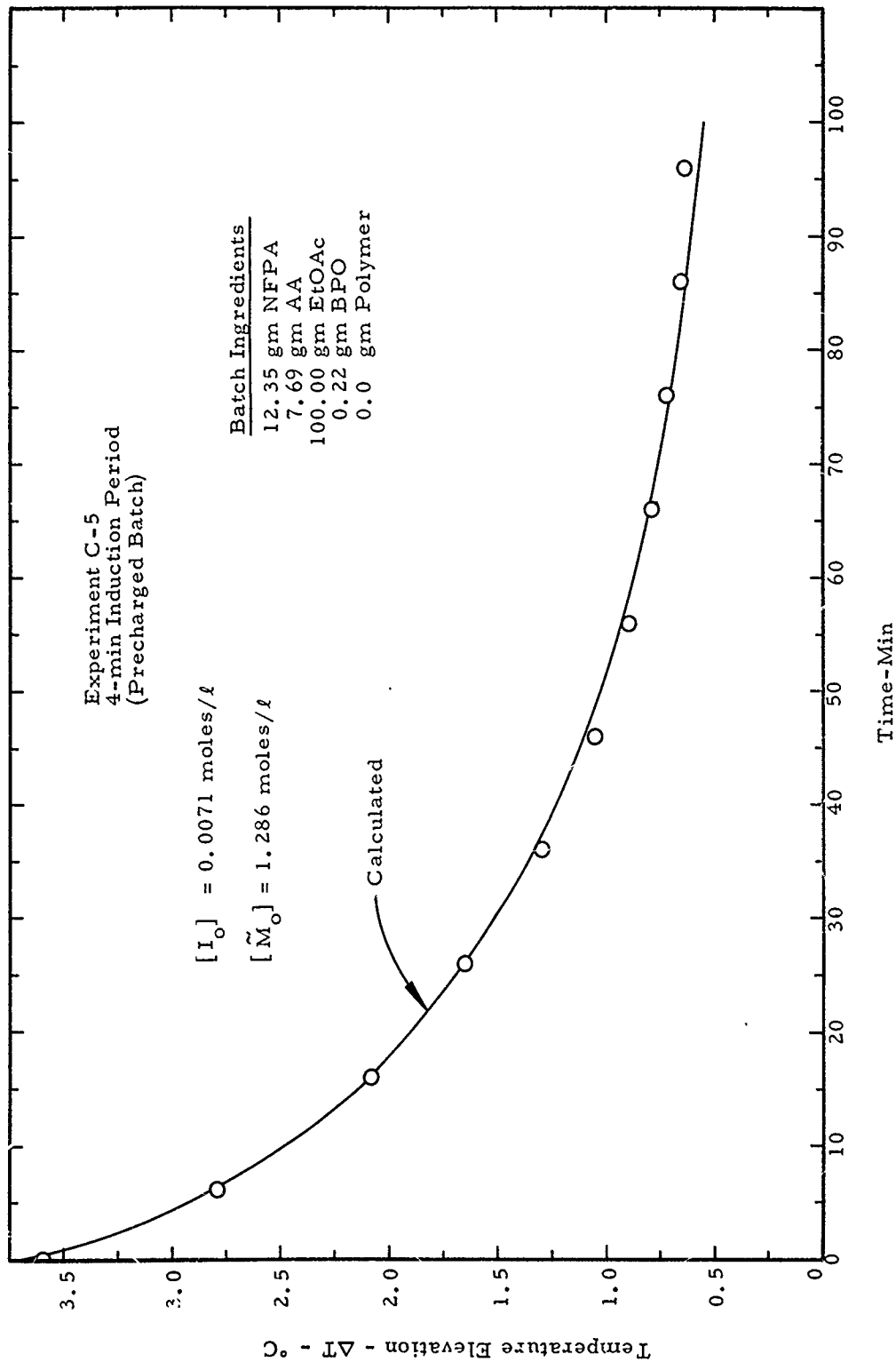Fig. 14 Polymer Fraction vs. Time by GC Analysis

Fig. 15 Temperature-Elevation-vs.-Time Data From Reflux Reactors
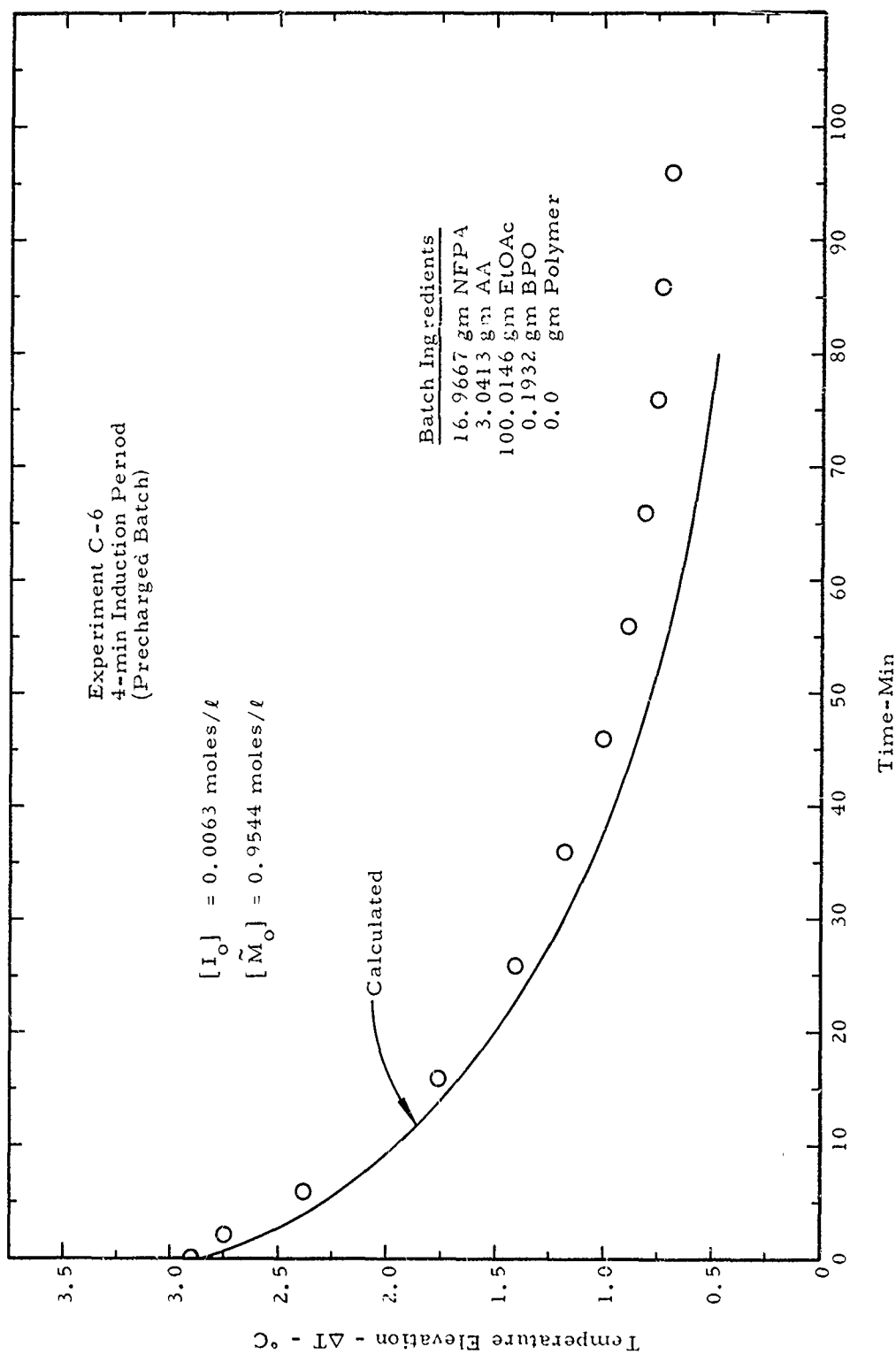
Fig. 16 Temperature-Elevation-vs-Time Data from Reflux Reactors
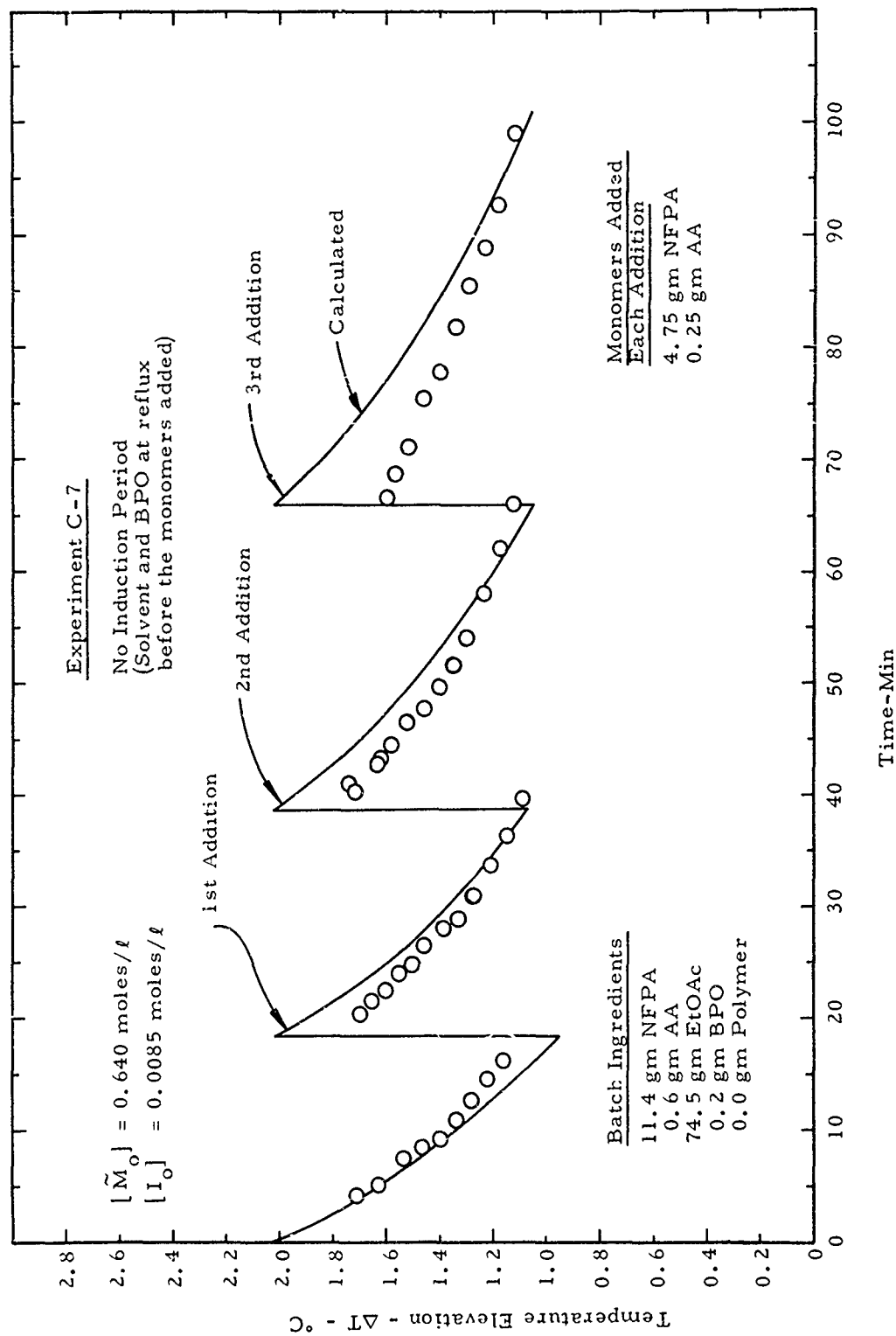
Fig. 17 Temperature-Elevation-vs-Time Data From Reflux Reactors, Preliminary-Addition Experiment
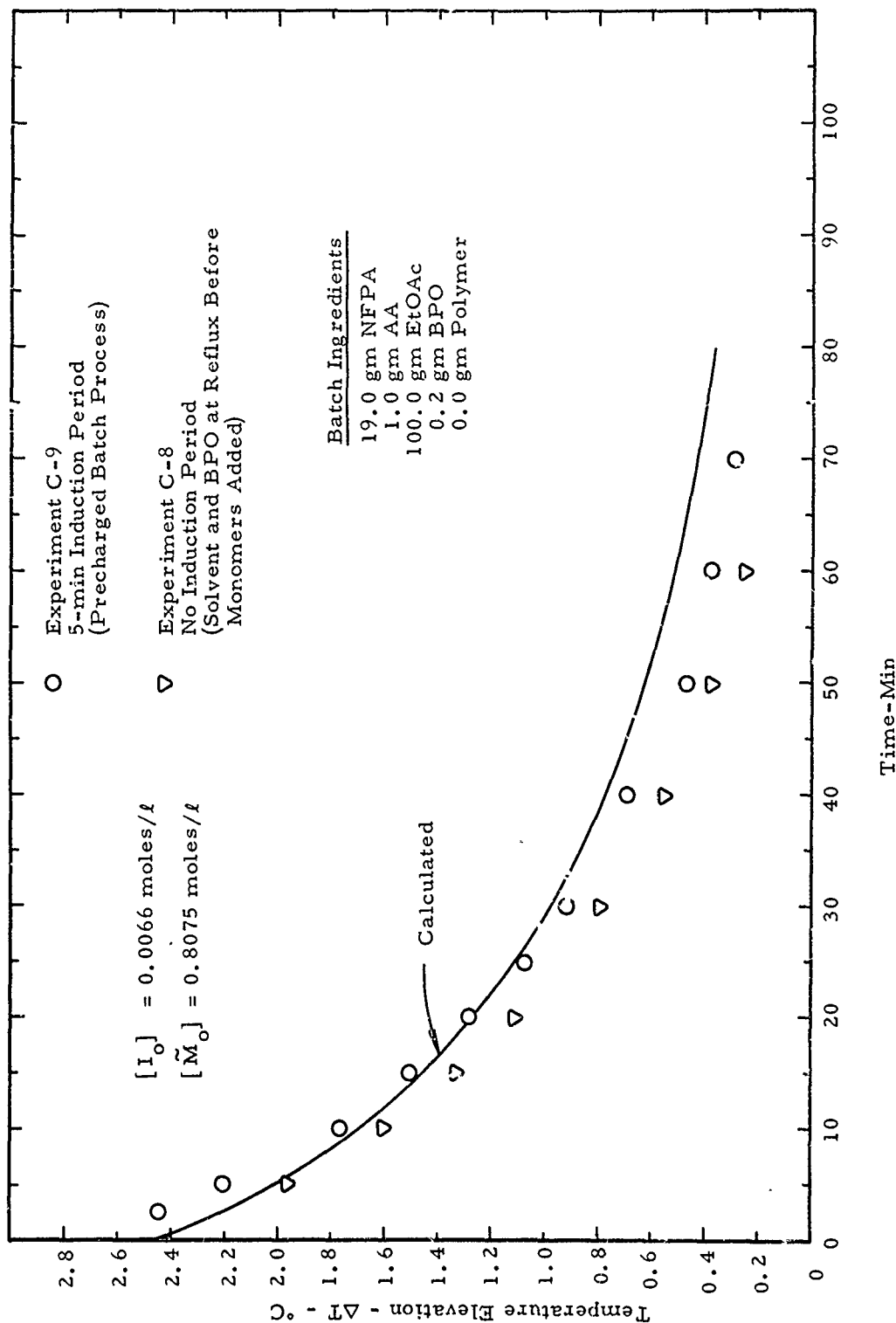
Fig. 18 Temperature-Elevation-vs-Time Data From Reflux Reactors

Fig. 19 Temperature-Elevation-vs-Time Data from Reflux Reactors

Experiment C-10
No Induction Period

Batch Ingredients
19.0 gm NFPA
1.0 gm AA
92.0 gm EtOAc
0.2 gm B?O
8.0 gm Polymer

$[I_o]$ = 0.0067 moles/ℓ
$[\tilde{M}_o]$ = 0.8311 moles/ℓ

Calculated

Time-Min

Temperature Elevation - ΔT - °C

Fig. 20 Temperature-Elevation-vs-Time Data from Reflux Reactors

Dilatometric Experiment at 75°C
5-Min Induction Period
(Precharged Batch Process)

$[\tilde{M}_o] = 0.374$ moles/ℓ

$[I_o] = 0.0099$ moles/ℓ

Batch Ingredients

0.48486 gm NFPA
0.0   gm AA
0.0144 gm BPO
5.0736 gm EtOAc
0.0   gm Polymer

Time-Min

Moles of Monomer/ℓ of Solution - $[\tilde{M}]$

Fig. 21 Monomer-Concentration-vs-Time Data from Dilatometric Data

Dilatometric Experiment at 70°C
60-Min Induction Period
(Precharged Batch Process)

$[\tilde{M}_o] = 0.370$ moles/ℓ
$[I_o] = 0.010$ moles/ℓ

Batch Ingredients

0.47892 gm NFPA
0.0   gm AA
0.01446 gm BPO
5.0778 gm EtOAc
0.0   gm Polymer

Time-Min

Moles of Monomer/Liter of Solution - $[\tilde{M}]$

0.4

0.3

0.2

0.1

0

0   20   40   60   80   100   120   140   160   180

Fig. 22 Monomer-Concentration-vs-Time Data from Dilatometric Data

observation is in agreement with the chain transfer hypothesis but in sharp disagreement with standard-radical-interaction behavior.
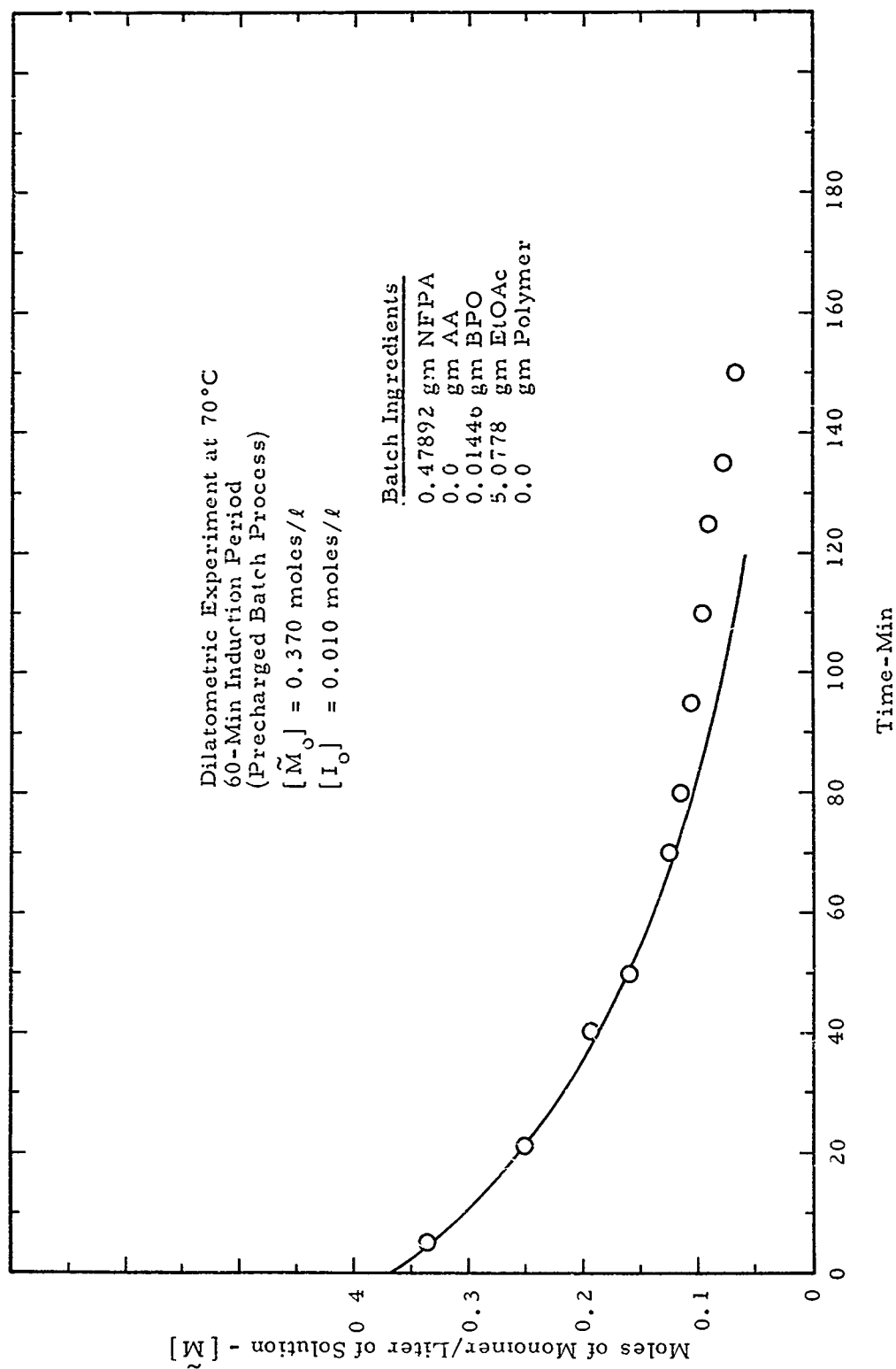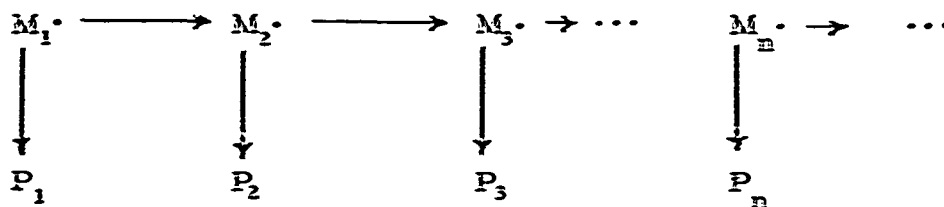
If consideration is given to the number-average molecular weight of the copolymer formed (e.g., M_n - 9,300 in experiment C-7, Fig. 17) in relation to the initiator decay rate and the polymerization history, the conclusion is reached that less than about one-fifth of the polymer molecule ends can contain an initiator fragment. Again this observation is compatible with chain-transfer behavior but in conflict with standard-radical-interaction behavior.

However, the assumption of chain-transfer termination must be considered as only a tentative or working hypothesis until considerably more research is done.

7.2   A Simple Model for Molecular-Weight Distribution

In a situation where chain transfer with the solvent is the dominant mode of termination, the following simple model will yield the distribution of molecular weights formed, assuming homopolymerization.

$$M_1\cdot \longrightarrow M_2\cdot \longrightarrow M_3\cdot \to \cdots \qquad M_n\cdot \to \quad \cdots$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\qquad\quad \downarrow$$

$$P_1 \qquad\qquad P_2 \qquad\qquad P_3 \qquad\qquad\quad P_n$$

In this sketch, $M_n\cdot$ represents a growing chain containing n monomer units and P_n represents a dead polymer chain containing n monomer units. In general $M_n\cdot$ can undergo two competing reactions: propagation or chain transfer. The propagation-reaction rate expression is

$$\frac{d[M_{n+1}\cdot]}{dt} = k_p [M_n\cdot][M] , \tag{13}$$

and the chain-transfer rate is

$$\frac{d[P_n]}{dt} = k_t [M_n \cdot] [S] \quad , \tag{14}$$

where the terms in brackets refer to concentrations, k_p is the propagation constant, k_t is the chain-transfer constant and $[S]$ is the fixed solvent concentration. It follows that the probability of propagation is

$$P_p = \frac{[M]}{[M] + K} \tag{15}$$

and that the probability of $M_n \cdot$ terminating through chain transfer is

$$P_t = \frac{K}{[M] + K} \quad , \tag{16}$$

where $K = k_t [S]/k_p$. The probability of $[M_1 \cdot]$ is assumed to be unity. The probability of forming a polymer molecule with n units becomes

$$P_{P_n} = \left\{ \frac{[M]}{[M] + K} \right\}^{n-1} \frac{K}{[M] + K} = \frac{K [M]^{n-1}}{([M] + K)^n} \quad , \tag{17}$$

and it follows that the sum of this probability from $n = 1$ to $n = \infty$ is unity. Eq. 17 provides the number distribution of molecules formed at a particular monomer concentration $[M]$. From this, the weight distribution can be obtained in normalized form as follows.

$$P_{W_n} = \frac{n P_{P_n}}{\sum\limits_{n=1}^{\infty} n P_{P_n}} \tag{18}$$

The chain length containing the greatest mass fraction n' can be obtained by differentiating the right side of Eq. 18 with respect to n and setting the result equal to zero. Since the denominator is a constant it may be disregarded, and it follows after some rearrangement that

$$e^{1/n'} = 1 \div \frac{K}{[M]} \quad . \tag{19}$$

For large n the approximation can be made that

$$e^{1/n'} \approx 1 \div \frac{1}{n'} \quad , \tag{20}$$

from which it follows that

$$n' \approx \frac{[M]}{K} \quad . \tag{21}$$

If $n > 5$, the error in Eq. 20 is less than 2%. The distributions obtained so far apply only for the polymer formed at a particular concentration of monomer. The distributions in the final product are of more practical interest. Consider a batch process in which the monomer concentration is originally $[M_0]$ and decreases to zero as the conversion to polymer goes to completion. The normalized number distribution in the final product becomes

$$q_n = \frac{\displaystyle\int_0^{M_0} p_{P_n} \, dM}{\displaystyle\sum_{n=1}^{\infty} \int_0^{M_0} p_{P_n} \, dM} \quad . \tag{22}$$

The normalized weight distribution in the final product becomes

$$Q_n = \frac{\displaystyle\int_0^{M_0} p_{W_n} \, dM}{\displaystyle\sum_{n=1}^{\infty} \int_0^{M_0} p_{W_n} \, dM} \quad . \tag{23}$$

The upper limits on the summations in Eqs. 18, 22, and 23 can be replaced by a sufficiently large finite integer without appreciable error resulting. The remaining integrals can be easily integrated numerically. Figs. 23 and 24 show calculated number and weight distributions formed for several fixed monomer concentrations. Figs. 25 and 26 show similar integrated results for a batch process. All calculations were based on the assumed value for K of 0.02 moles/ℓ. This value was selected because it gave number-average molecular weights in fair agreement with the observed results. An interesting research project would be to try to relate this chain-transfer-termination model to measurable properties of the polymer.

8.0 DEVELOPMENT OF INCREMENTAL-ADDITION PROCESS

Two objectives were considered important in this copolymer-process-development work. The first was to increase productivity by increasing the final polymer concentration in the reactor solution. The second objective was to achieve proper control over the copolymer compositional uniformity and molecular weight distribution. Implied in the second objective is a satisfactory trade-off between propellant physical properties and processing and mixing difficulties. Both of these objectives can be met to a high degree by the use of an incremental-addition process (IAP). In this process, a charge of monomers is added to the reactor and a portion of the polymerization is allowed to occur. Then another charge of monomers is added to restore the monomer concentration to the original level and additional polymerization occurs. The addition procedure can be repeated several times.

If a pre-charged batch process is used to obtain a high final polymer concentration in the reactor solution, high monomer concentrations must be used. These high concentrations are undesirable because they increase the probability of a runaway reaction which could produce a considerable exotherm. Such exotherms must be avoided since NFPA is an explosive. By using the incremental addition technique, lower monomer concentrations can be used to achieve a high final polymer concentration.
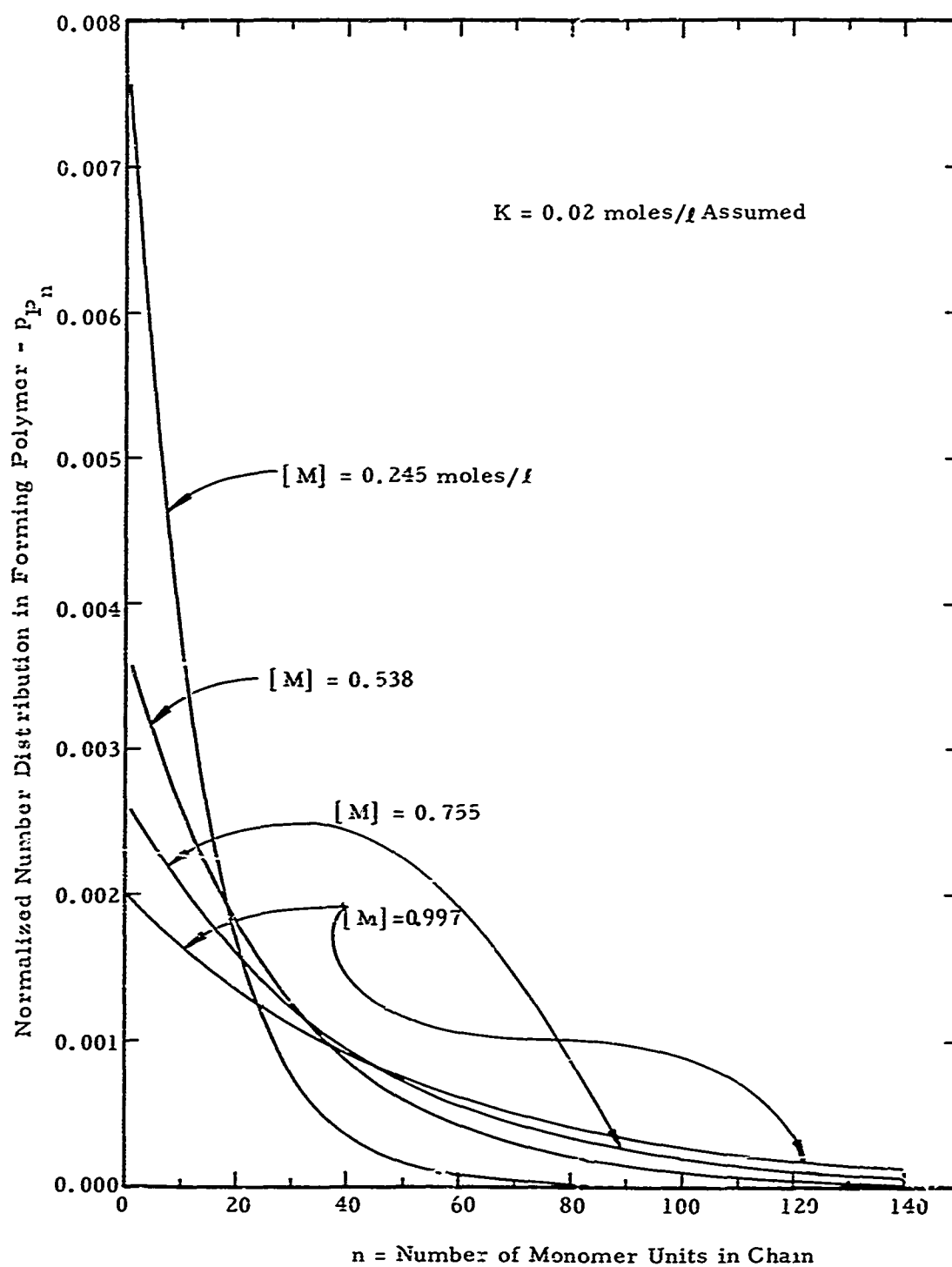
Fig. 23 Calculated Number Distributions in Forming Polymer
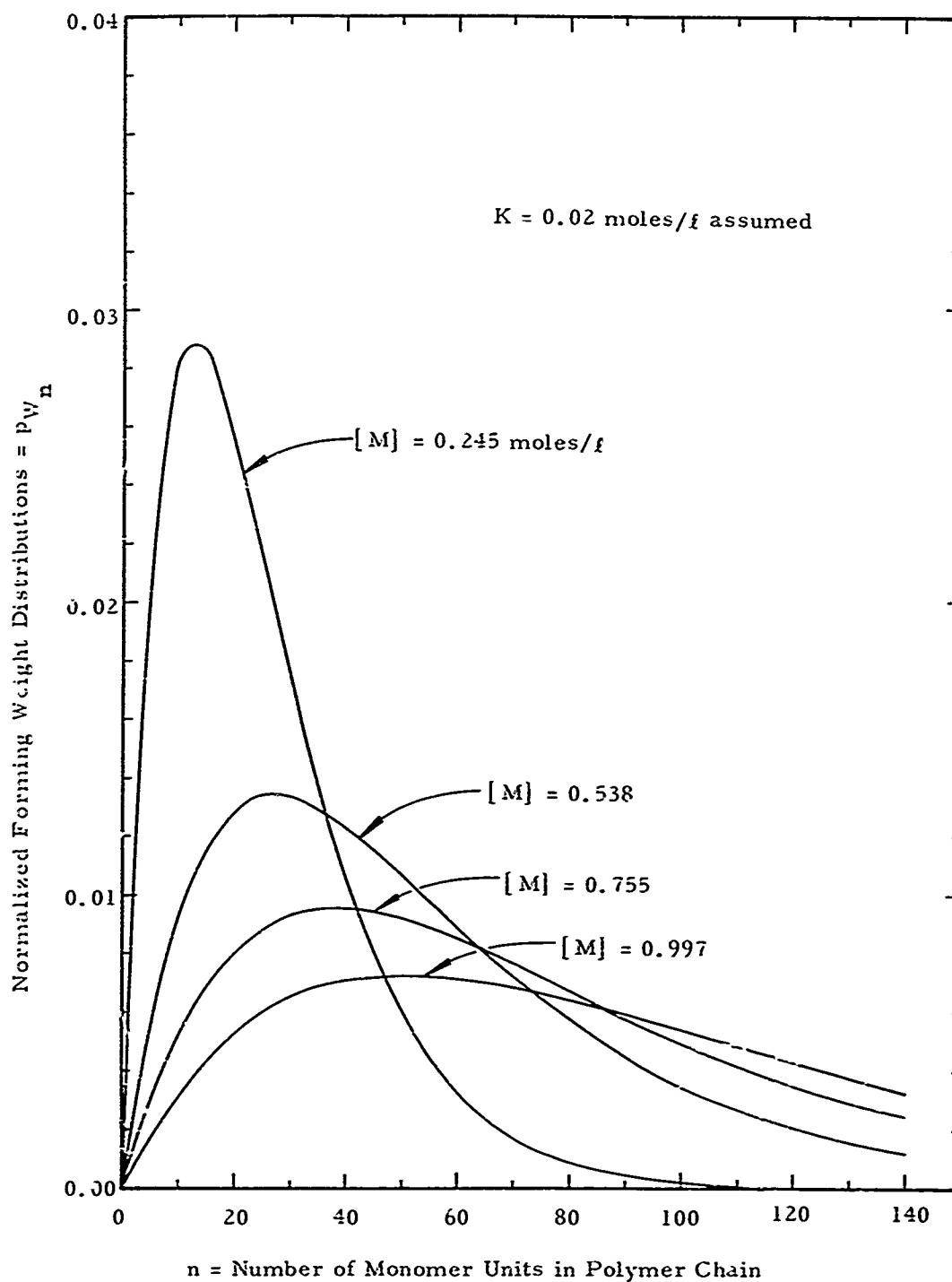
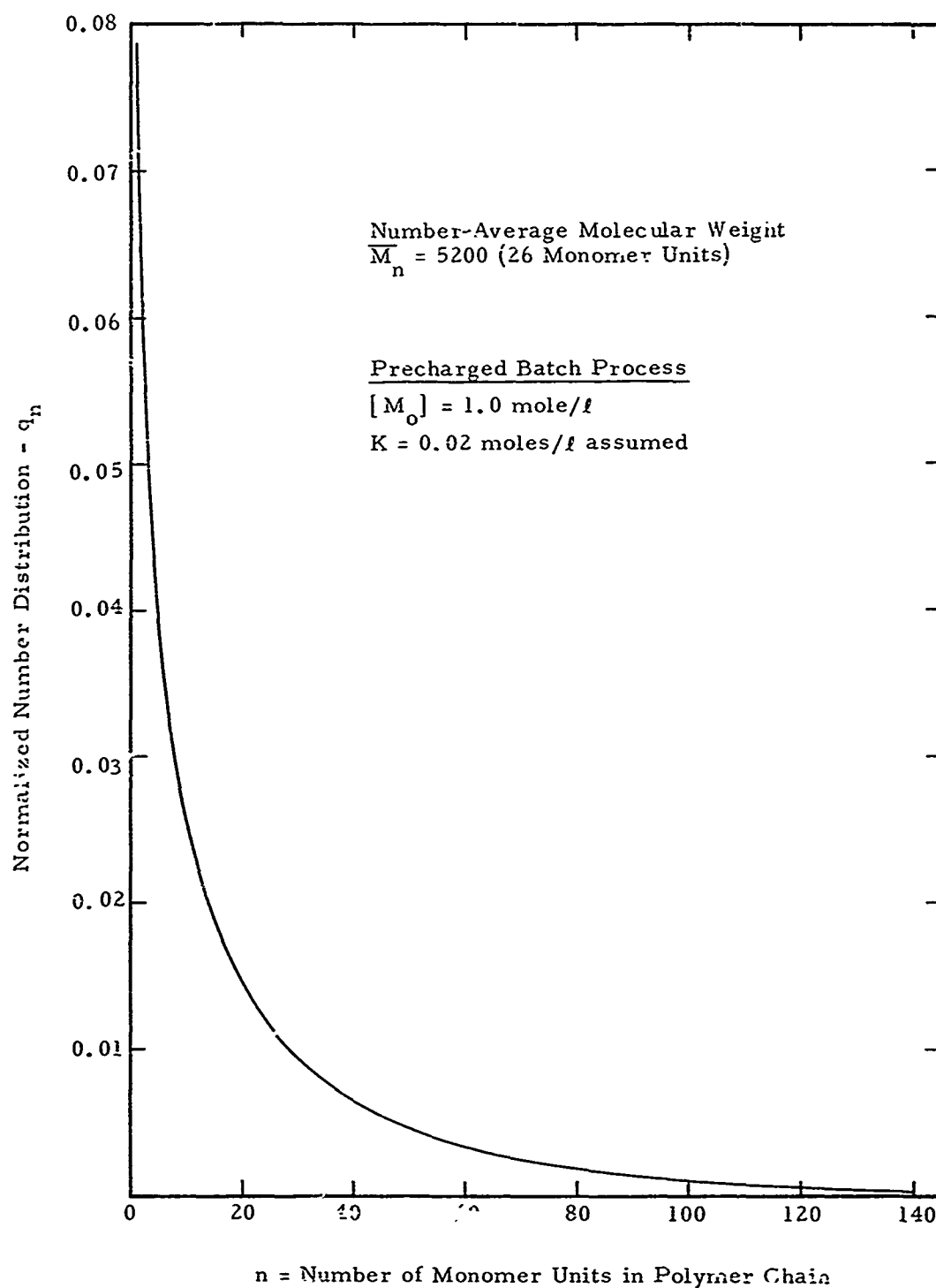Fig. 24 Calculated Normalized Weight Distributions for Particular Monomer Concentrations

Fig. 25 Calculated Normalized Number Distribution Integrated Over Varying
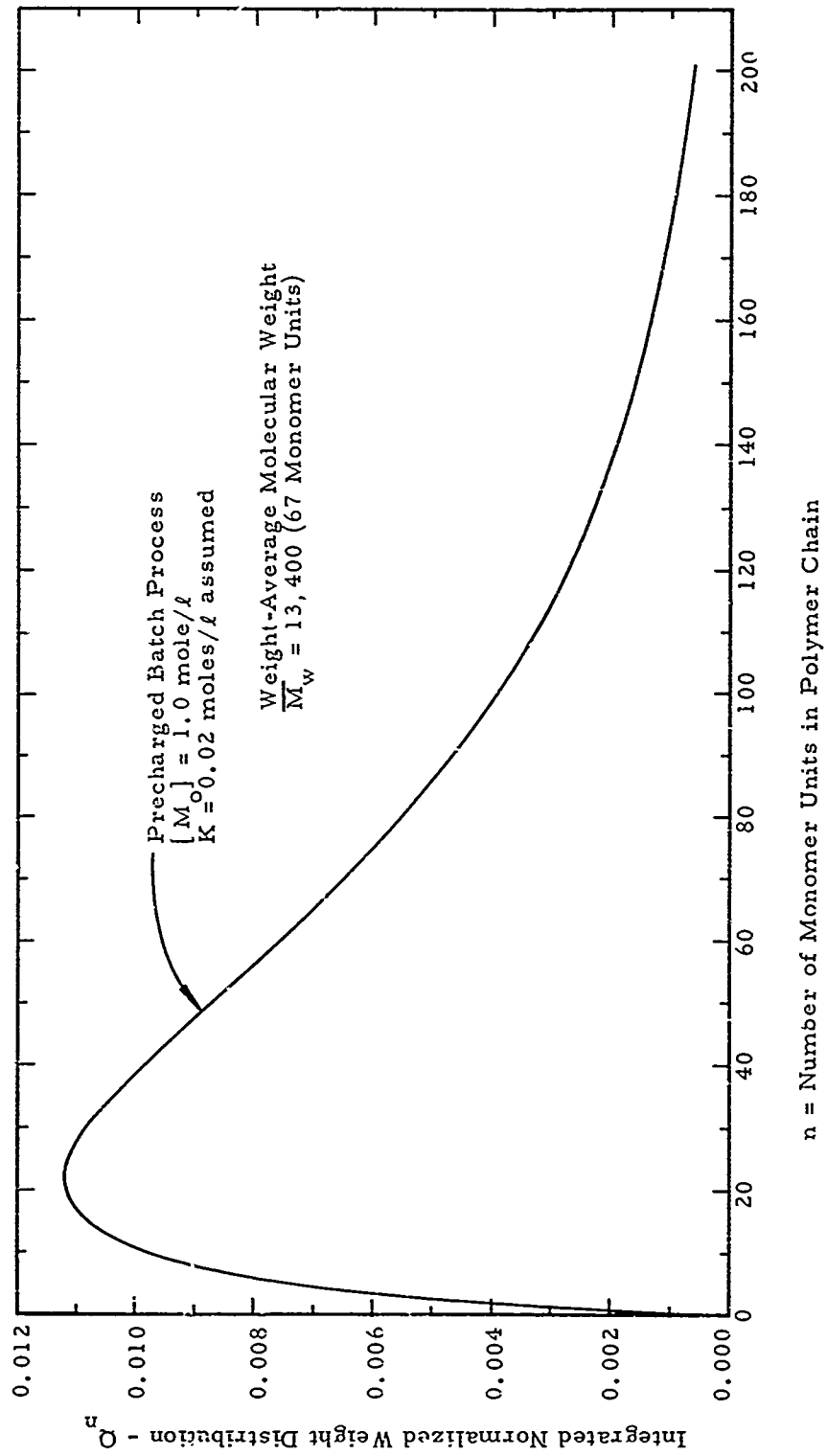Monomer Concentrations

Fig. 26   Calculated Normalized Weight Distribution Integrated Over Varying Monomer Concentrations

The polymer tends to form a copolymer with fairly good compositional uniformity as shown in Figs. 7 and 8. For this reason it was decided to mix the NFPA and AA together and to add portions of this mixture to the reactor. While it is theoretically possible to obtain a slight improvement in compositional uniformity by using a different ratio of NFPA/AA in each addition, the use of this technique was not felt to be worth the extra effort in this case. Previous work has led to the selection of the 96/4 NFPA/AA weight-ratio copolymer and this ratio was used in developing the IAP.

The molecular weight of the copolymer is believed to be determined primarily by chain-transfer chain-growth termination with the EtOAc solvent as discussed previously. Accordingly, to a first approximation, the molecular weight of polymer being formed at any time is proportional to the monomer/solvent ratio at the time the polymer is formed. (A polymer chain is considered to be formed instantaneously for practical purposes.) In fact, the peak of the molecular-weight distribution of polymer being formed at any time is directly proportional to this ratio at the time as can be seen in Eq. 21. Since the temperature elevation has also been shown to be related to the monomer/solvent ratio, the temperature elevation serves as an indication of the molecular weight of the polymer being formed. The IAP offers a means of controlling the monomer concentration and hence the molecular weight distribution.

Several processes were studied in selecting the particular IAP to be scaled up. Three of these which will be discussed in detail are listed below: (1) the standard pre-charged batch process (24% final polymer concentration), (2) a 30%-final-polymer-concentration IAP (30%-IAP) having a relatively low molecular weight, and (3) a 39%-final-polymer-concentration IAP (39%-IAP) having a relatively high molecular weight. The third process was selected for scaleup since it proved to be the best for making RH-SE-103 propellant, the composition for which the copolymer was developed (see Table I). It is expected that the copolymer made by this particular IAP might not be optimum for similar propellants with different solid

loadings, ammonium perchlorate (AP) particle sizes, or TVOPA[1]/
copolymer ratios.

<div align="center">Table I</div>

<div align="center">Composition of RH-SE-103 Propellant</div>

	Percent by Weight [†]
Aluminum	15
AP (55 μ)	46[††]
TVOPA	26
NFPA/AA Copolymer (96/4)	13
	100 Total

[†] Unox® * 221 di-epoxide curing agent is added to the above
   mixture. Typically 1-1/2 parts of curing agent are added for each
   100 parts above which results in an epoxide/acid equivalence ratio
   of 1.5/1. (An assay on the curing agent indicates approximately
   139 gm per molar equivalence of epoxide.)

[††] The AP contains 1% Alon-C®** which serves as a stabilizer and an
   anti-caking agent.

Plots of calculated temperature elevation versus conversion
for each of these three processes are shown in Fig. 27. To a first
approximation, these plots serve as a picture of the molecular
weight of the polymer being formed since the temperature elevation
and polymer molecular weight have been shown above to be directly
related. The selection of the initiator concentration and the addition
times was accomplished by using the polymerization-rate model
previously described.

In making copolymer by the standard batch process, the
ingredients are charged to the reactor, heat is applied, and the
reactor is refluxed overnight at atmospheric-pressure. The in-
gredients are mixed with the following weight percentages: 75.72%

[1] TVOPA: 1, 2, 3-tris[α, β-bis(difluoramino)ethoxy] propane, a
   plasticizer.
* Union Carbide Corporation, 270 Park Avenue, New York, N.Y.
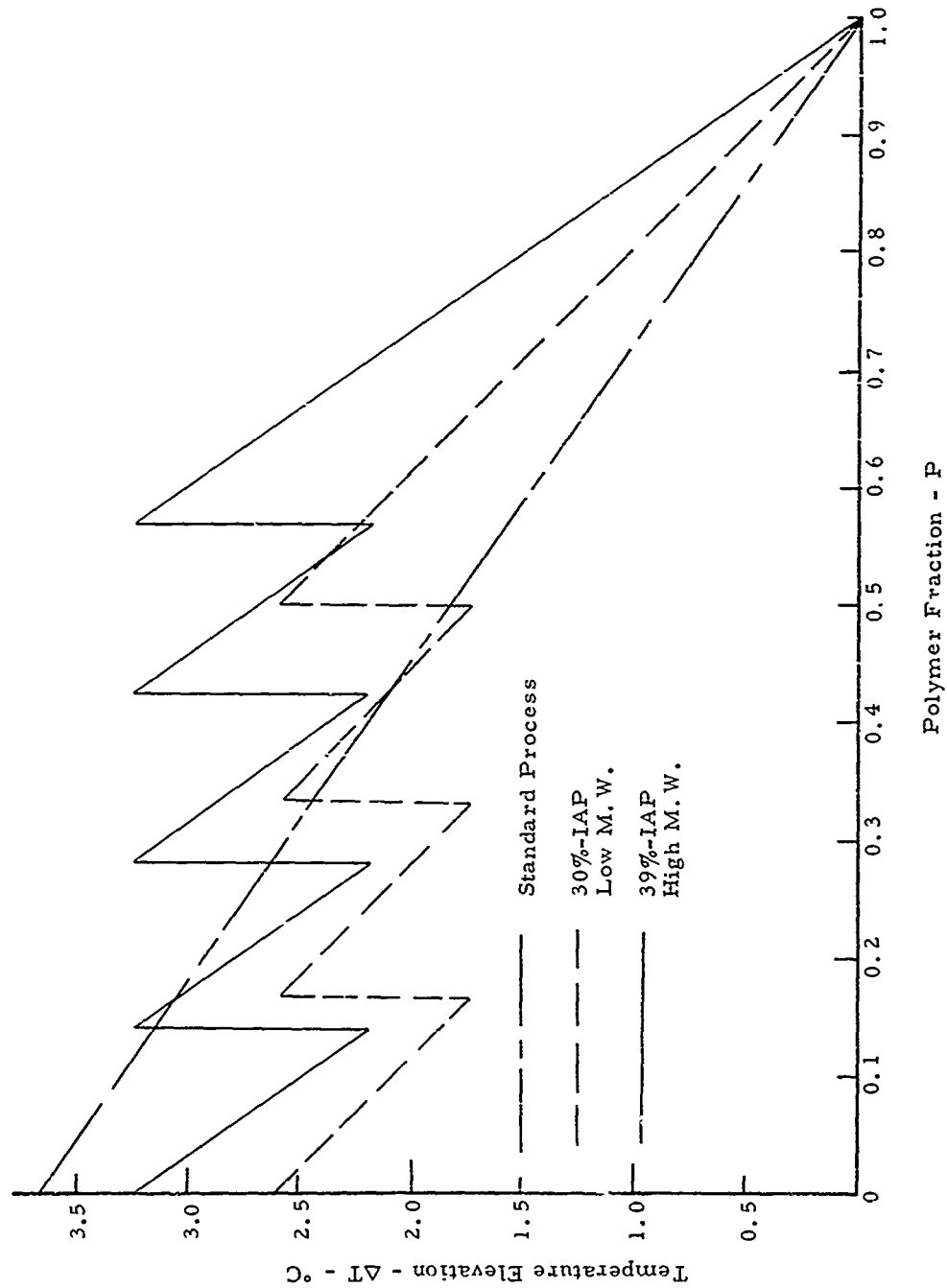** Cabot Corporation, 125 High Street, Boston, Mass.

Fig. 27 Temperature Elevation vs Conversion (An Indication of the Molecular Weight of the Polymer as it Forms)

EtOAc, 23.08% NFPA, 0.96% AA, and 0.24% BPO. The overnight reflux is necessary in order to consume the BPO; residual BPO has been shown to cause fissuring problems in propellant—probably from the carbon dioxide which is released by initiator decomposition.

The procedure for carrying out the IAP is slightly more complicated. The EtOAc solvent and the BPO initiator are placed in the reactor and refluxed at atmospheric pressure for at least 5 min. During this period, inhibitors in the solvent such as dissolved oxygen are consumed and the induction period which occurs after the monomers are added is greatly reduced. The induction period after a monomer addition using the above procedure is about 1 min or less, which is a small fraction of the time between additions. Fig. 28 shows the calculated temperature elevation history for the 30%-IAP along with the batch recipe. Similar data for the 39%-IAP is given in Fig. 29. After the final monomer addition step, the reflux is continued overnight as for the standard process.

A 35%-IAP, which was identical with the 39%-IAP except that the last addition was omitted, was also studied. A summary of data for the copolymers made by the various recipes is given in Table II. Included in the table are viscosity data on the 2/1 TVOPA/copolymer weight-ratio binder mixture (referred to as the TP binder mixture or simply TP). The intrinsic viscosity included in the table is felt to be the best indication of relative copolymer weight-average molecular weight which is important to propellant physical properties. Two number-average molecular weights are given. The first value was obtained by stripping all of the solvent from the copolymer and measuring the number-average weight by use of a Mechrolab[1] Model 301 vapor-pressure osmometer. The second value was obtained by first precipitating the polymer in pentane, which eliminates 1-2% by weight of the polymer by leaving a low molecular-weight fraction dissolved in the pentane. The polymer was then redissolved and stripped and the number-average molecular weight measured. The

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[1] Mechrolab, Inc., 1062 Linda Vista Avenue, Mountain View, Calif.
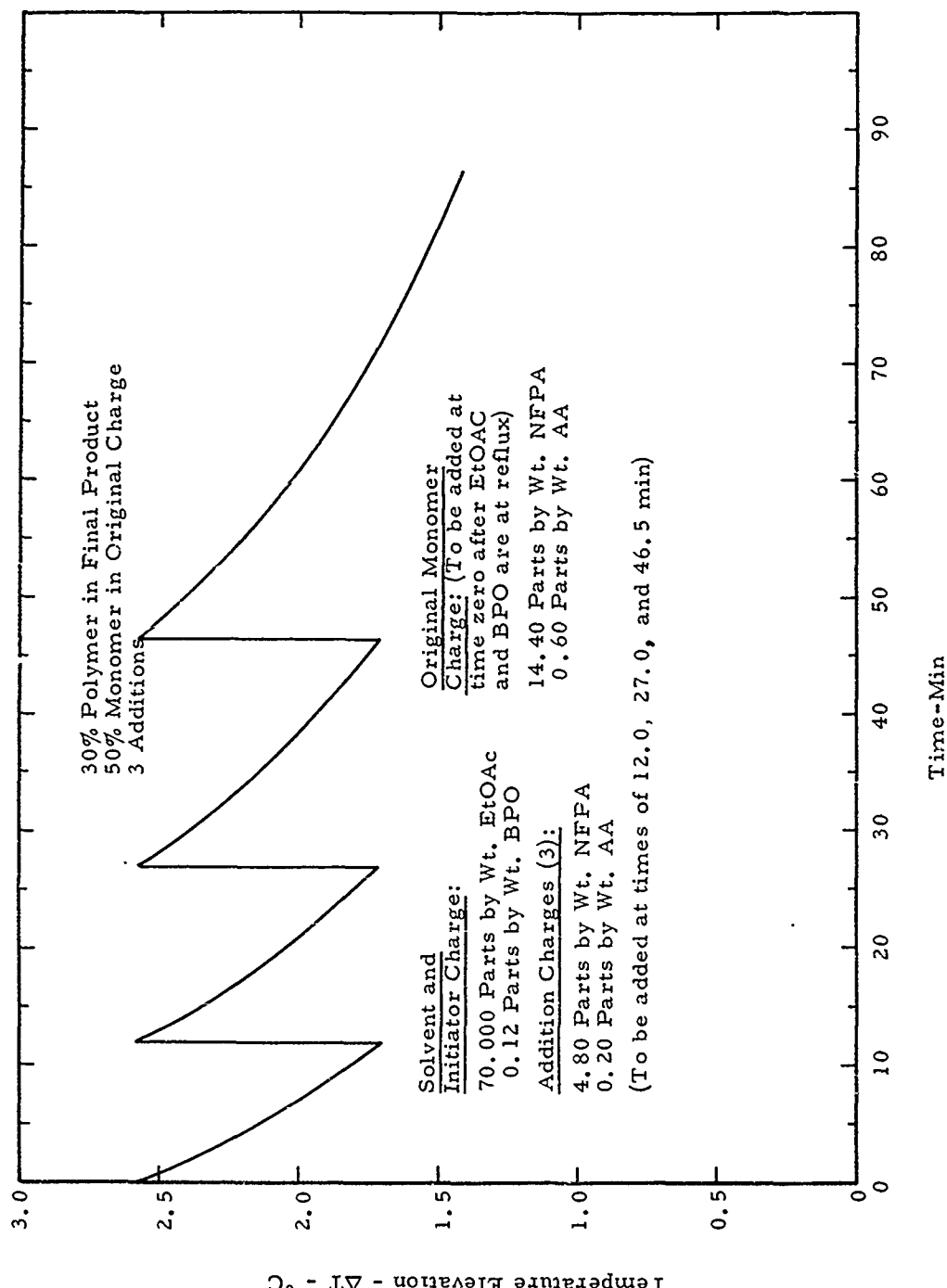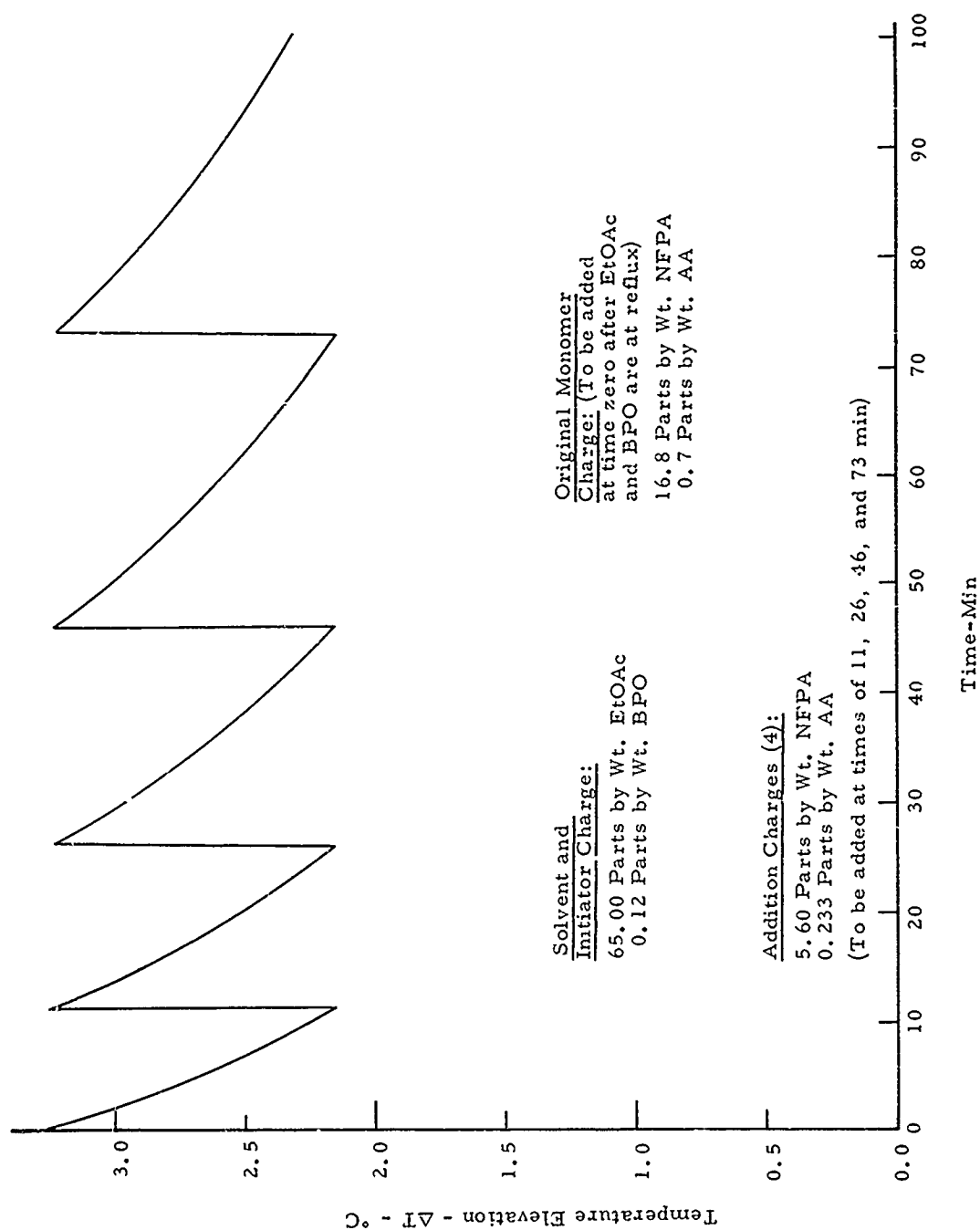
Fig. 28 Temperature-Elevation History, 30%-IAP

Fig. 29 Temperature-Elevation History, 39%-IAP

first technique probably includes a small amount of residual monomer
and probably results in a lower-than-actual value. The second
technique has probably not included a significant number of low-
molecular-weight polymer molecules and probably results in a high
value. The true number-average molecular weight is probably
between the two figures given in the table. The large difference
between the two number-average molecular weights shows that a
significant amount of low-molecular-weight polymer was present.
Additional experimental work is being done in the area of copolymer
molecular-weight distributions using gel-permeation chromatography
and through careful fractionations of the copolymer and will be
included in future reports.

<u>Table II</u>

<u>Copolymer Data</u>

		Standard Process	30%-IAP	35%-IAP	39%-IAP
Number-Average Molecular Weight	Stripped only	≈6000	≈6000	≈6000	≈6000
	Precipitated in pentane and stripped	≈9300	-	-	≈12000
Intrinsic Viscosity (deciliters/gm)		0.21	0.22	0.31	≈0.40
TP-Binder Viscosity at 100°F, KP		0.10	0.07	0.30	0.41

Additional TP-binder viscosity data as a function of temperature
is given in Fig. 30, and similar propellant-slurry viscosity data is
given in Fig. 31. The average AP particle size was 55 μ except in
one instance where 15 μ AP was used with the 39%-IAP copolymer.
The only condition for which mixing problems might exist is the one
instance with the 15 μ AP. The relationship between TP-binder
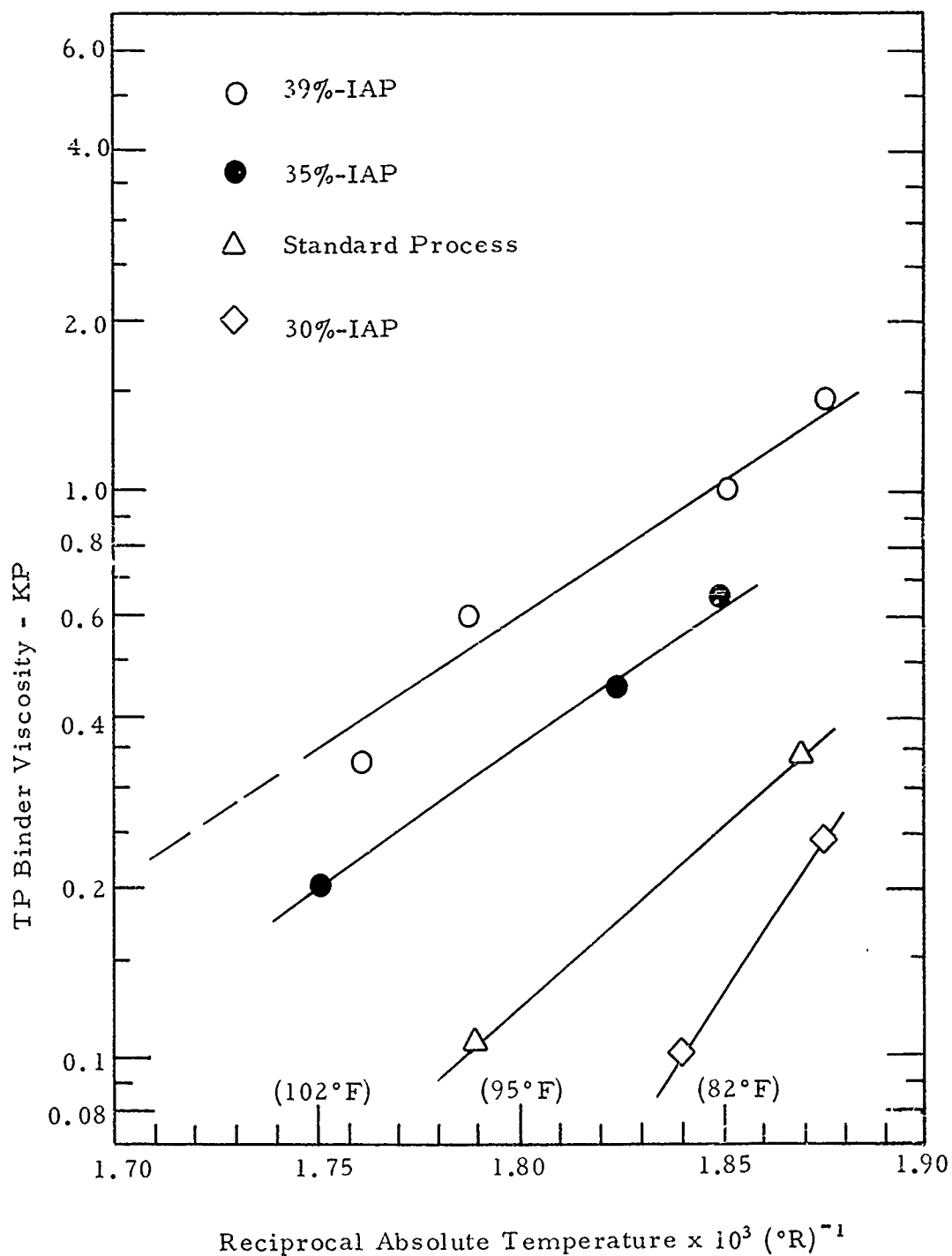viscosity and propellant-slurry viscosity when the copolymer recipe

Fig. 30 Propellant Binder Viscosity, 2/1 TVOPA/Copolymer Weight
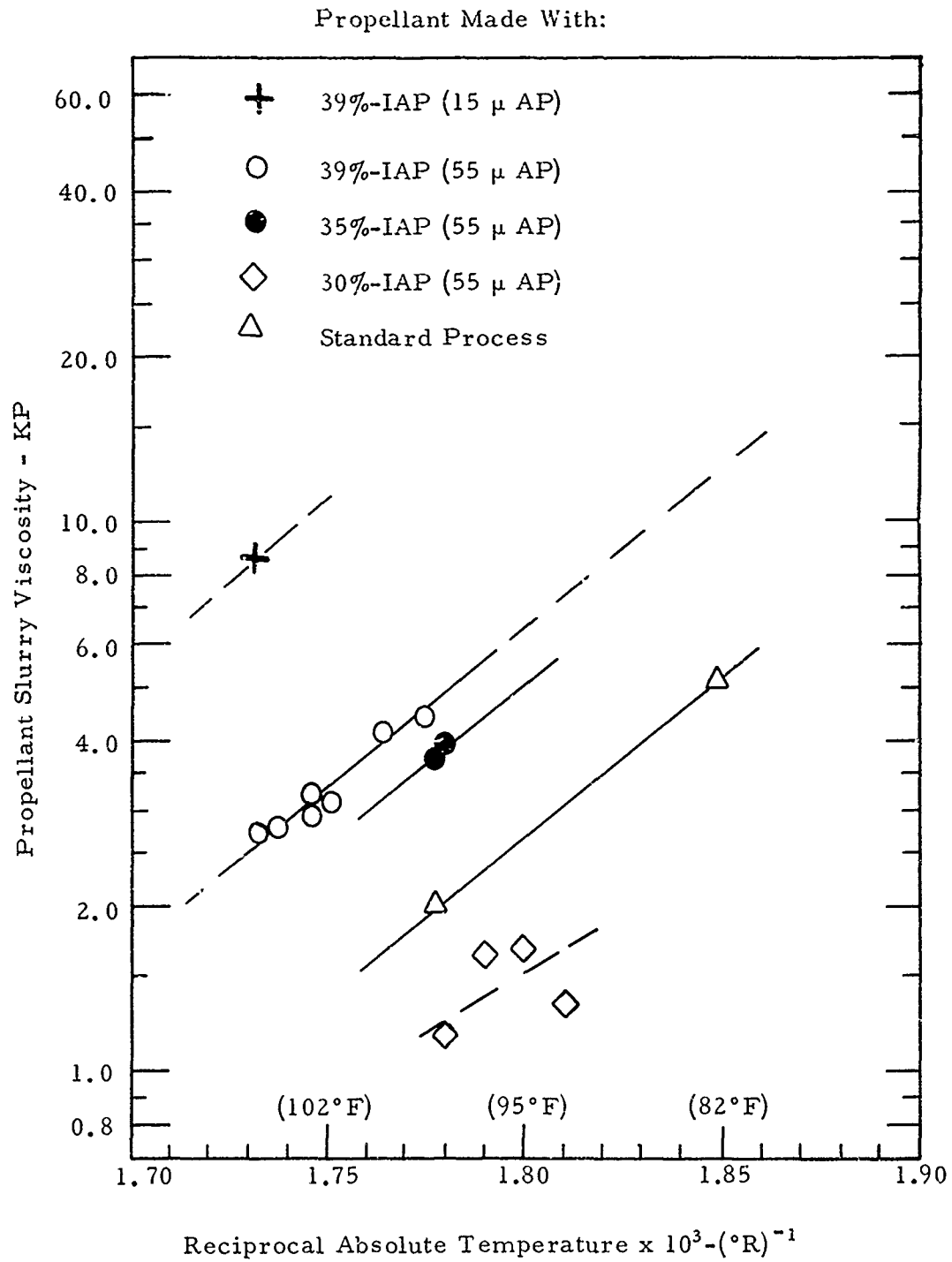Ratio

Fig. 31 Propellant Slurry Viscosity

and the AP particle size are kept constant is shown in Fig. 32. The
data in Fig. 32 were obtained by reading data from the curves in
Figs. 30 and 31 at comparable temperatures; the linear relationships
result from the linear treatment given the data in Figs. 30 and 31 and
are obviously somewhat tenuous.

The final polymer concentration in the reactor must be low
enough to allow adequate mechanical stirring with a comfortable
factor of safety. In selecting this value, considerable judgment
must be exercised based on the available experience. This con-
centration was increased as the process was modified and additional
increases could probably be made over the 39% value, the highest value
attempted to date. Fig. 33 shows the viscosity of the 35%-IAP co-
polymer and EtOAc solvent as a function of copolymer concentration.
From this figure it can be seen that the solution viscosity increases
rapidly when the copolymer concentration reaches approximately
the 50% level. In addition to the viscosity limitation, the polymeri-
zation rate decreases significantly with high polymer concentration
as can be seen by reviewing Eqs. 10 and 12. For this reason, a
nearly complete conversion of monomer to polymer might not be
obtained from the overnight reflux if the final concentration were
greatly increased above the 39% level.

Comparative propellant physical properties are shown in Fig. 34.
In this figure the maximum stress and strain at maximum stress are
shown as a function of temperature. This data was obtained with
standard ICRPG test specimens in a uniaxial extension test at
a crosshead-separation rate of 2 in./min.[1] The propellant made from
the 39%-IAP copolymer obviously has the best combination of physical
properties. This figure demonstrates the very large effect that the
copolymer has on propellant physical properties. The epoxide/acid
equivalence ratio has an important effect, although perhaps not as great an
effect as the copolymer, and the AP particle size is also important.

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[1] Interagency Chemical Rocket Propulsion Group (ICRPG) Solid
Propellant Mechanical Behavior Manual, Section 4.3, June
1963.

① Standard Process (55 μ AP)

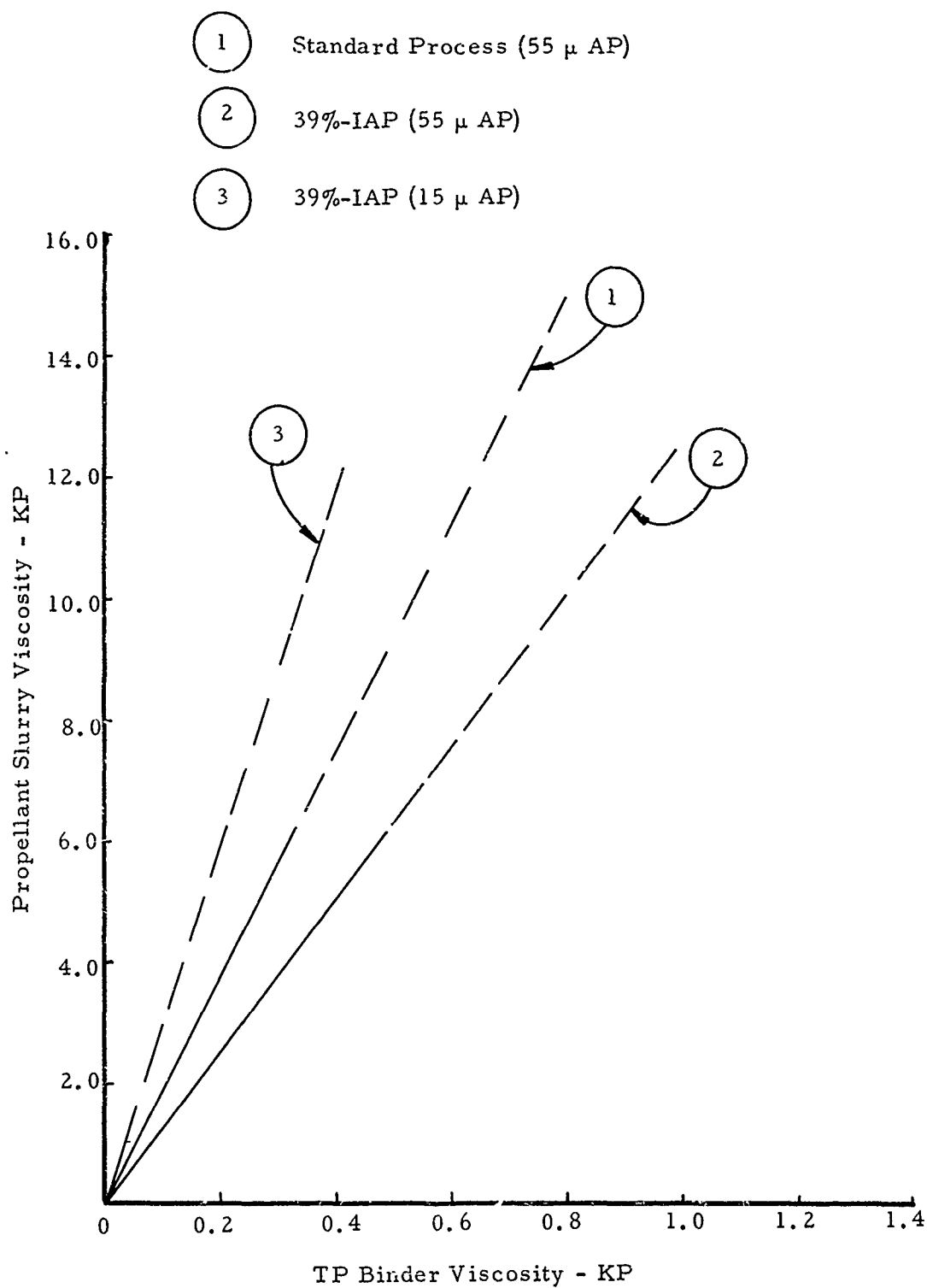② 39%-IAP (55 μ AP)

③ 39%-IAP (15 μ AP)

Fig. 32 The Relationship Between Propellant-Slur·y and TP-Binder Viscosities

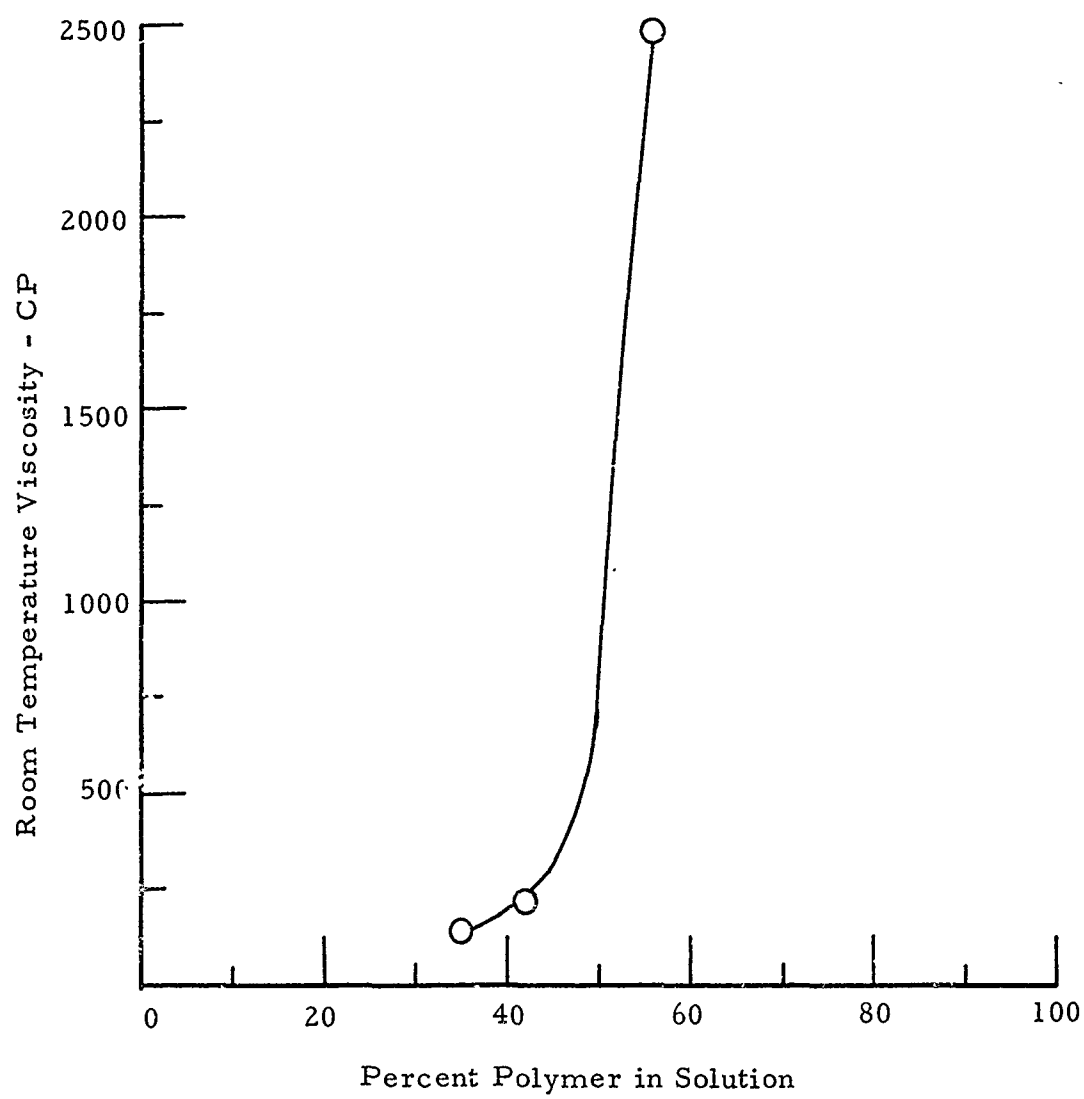Copolymer Made by the 35%-IAP

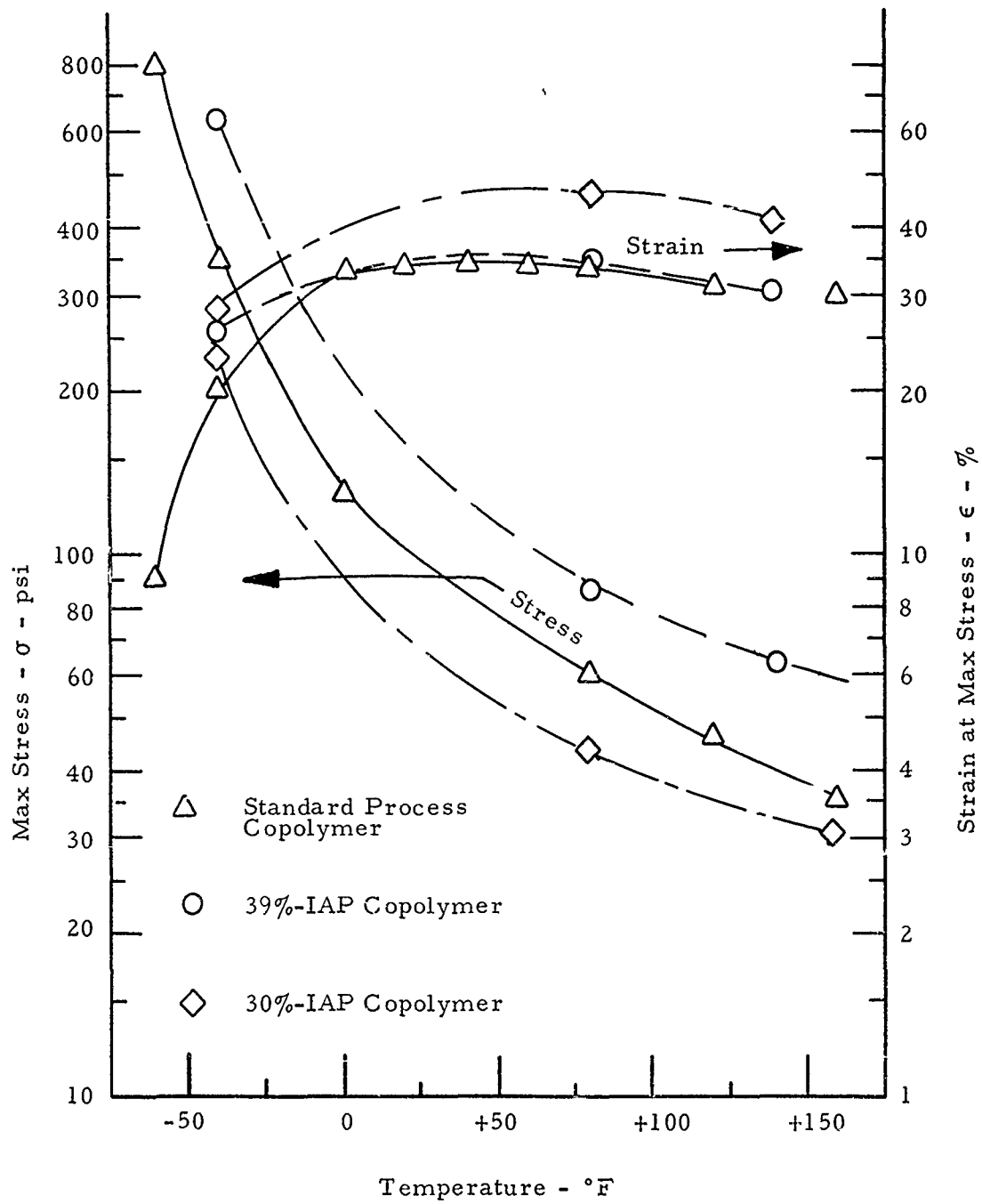Fig. 33 Relationship of Copolymer-Reactor-Solution Viscosity to Concentration

Fig. 34 Comparative Physical Properties, RH-SE-103 Propellant, 55 μ AP, 1.5 Epoxide/Acid Equivalence Ratio

For example, propellant made with the 39%-IAP copolymer and 15 μ AP (rather than 55 μ) had the following physical properties: $\left[\frac{\sigma(psi)}{\epsilon(\%)}\right]_{max} = 838/18$ at -40°F; $\left[\frac{\sigma(psi)}{\epsilon(\%)}\right]_{max} = 114/24$ at 77°F; and $\left[\frac{\sigma(psi)}{\epsilon(\%)}\right]_{max} = 73/22$ at +140°F.

If the TVOPA/copolymer ratio is held to within a few percent of the specified value, and the TP binder is stripped to approximately 99.5% nonvolatiles, the propellant physical properties have been found to be very reproducible.

A strong correlation is observed between propellant fissuring behavior and high-temperature mechanical strength. Propellant made from the 30%-IAP copolymer, which had the lowest strength (see Fig. 34), had a time-to-fissure of 100 hr in the 2-in. cube, 80°C (176°F) fissuring test. Propellant made from the standard-process copolymer, which has an intermediate strength, fissured at 450 hr. Propellant made from the 39%-IAP copolymer which has the highest strength did not fissure in 1500 hr at the elevated temperature. In the last case, it is expected that the 2-in. cubes might last indefinitely at 80°C because an equilibrium condition between the gas generation and gas escape by diffusion is believed to have been established.

The high-temperature, mechanical-property aging characteristics of RH-SE-103 propellant are an area of concern, but preliminary data from propellant made with the 39%-IAP copolymer looks promising. Two-inch propellant cubes which were subjected to 1500-hr storage at 80°C without fissuring were cut into small tensile specimens after the termination of the fissuring tests. The maximum stress at 77°F was found to be 90 psi which compares with 86 psi before high-temperature storage. No reliable strain data could be obtained from the small samples, but it seems unlikely that the strain capability could have changed greatly without the stress also changing. Fifteen hundred hours (or 63 days) at 80°C is a severe test for fissuring or mechanical property storage, and the 2-in. cubes appeared to be as

sound as when placed in the oven. Propellant cubes made from the standard-process copolymer became hard and brittle after similar storage, and, of course, they fissured after about 450 hr. The difference in the fissuring behavior is attributed to the higher mechanical strength. No explanation is offered for the improved mechanical-property stability.

It is felt that improved control over the molecular-weight distribution was obtained in the new process and was responsible for the significantly improved propellant properties. Additional experiments are planned in which the 39%-IAP will be stopped at about 70% conversion. The polymer will be removed and made into propellant. It is expected that using this technique (which eliminates the low-molecular-weight-molecules produced during the tail end of the reaction) will yield additional improvements in propellant properties, but substantial processing difficulties and yield losses will also result. The distributions obtained in EtOAc solvent will always be fairly broad due to the polymer characteristics associated with chain-transfer chain-growth termination. Therefore, if suitable solvents could be found which would give radical-interaction chain-growth termination more typical of acrylics, it would be theoretically possible to make NFPA/AA copolymers having more desirable characteristics. Techniques similar to those suggested by Hoffmann et al.[10] might be useful in this case.

The 39%-IAP copolymer described above has been selected as being the best copolymer for RH-SE-103 propellant, and this process is being adopted as the standard process for making the NFPA/AA copolymer. Earlier in the report, the compositional uniformity of the copolymer was discussed. Fig. 35 shows the calculated uniformity versus conversion for the 39%-IAP copolymer. Theoretical number-average run lengths of NFPA and AA molecules in the chain versus conversion are shown in Fig. 36. The calculations for these figures were made using the reactivity ratios $r_1 = 0.42$ and $r_2 = 0.75$ as described previously.

96/4 NFPA/AA Weight Ratio

$r_1 = 0.42$, $r_2 = 0.75$ Assumed in Calculations
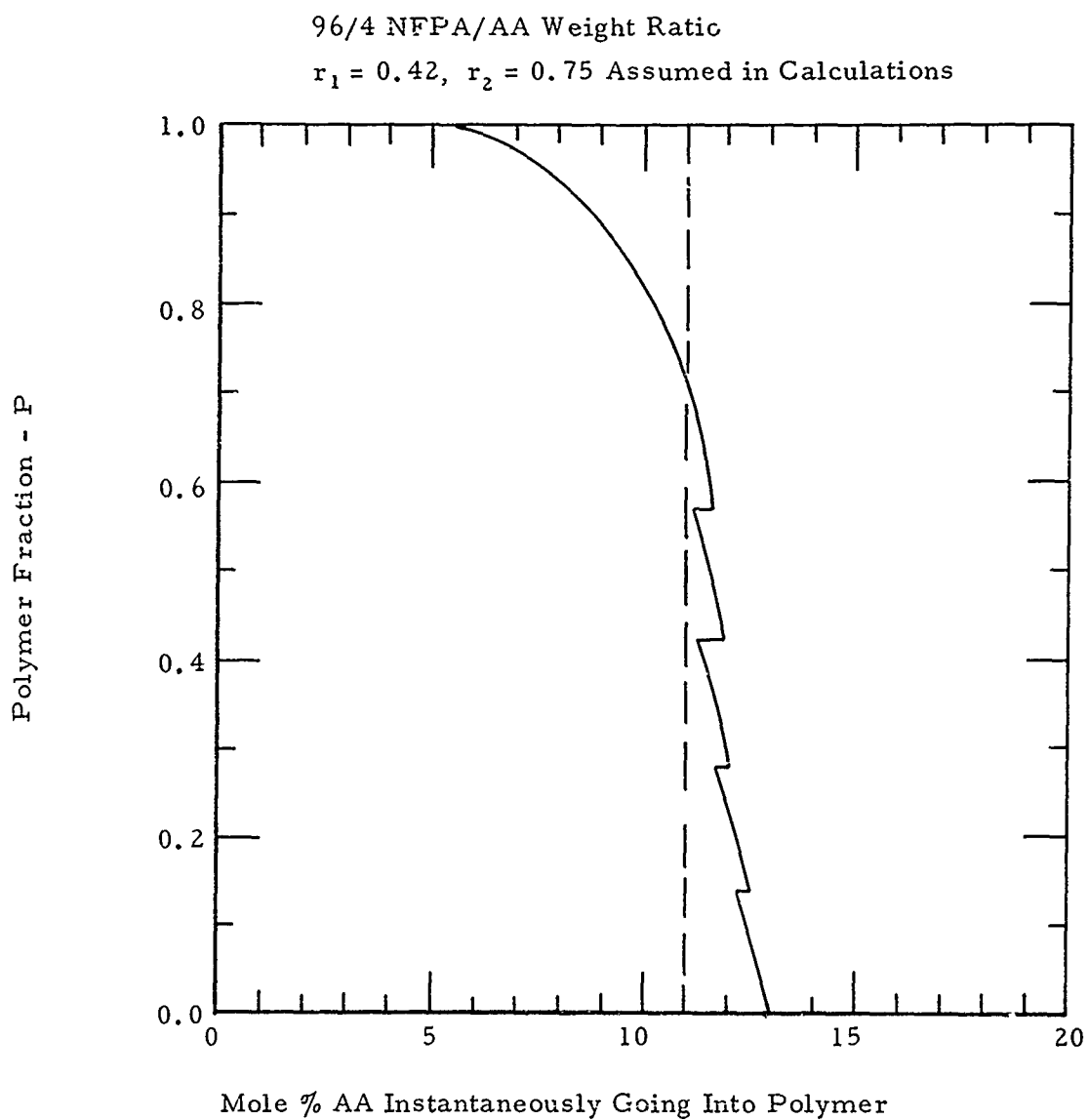
Fig. 35 Composition of Forming Polymer, 39%-IAP

96/4 NFPA/AA Weight Ratio

$r_1 = 0.42$, $r_2 = 0.75$ Assumed in Calculations

NFPA

AA

Polymer Fraction - P

Number-Average Run Length of Monomer Units in Polymer Chains
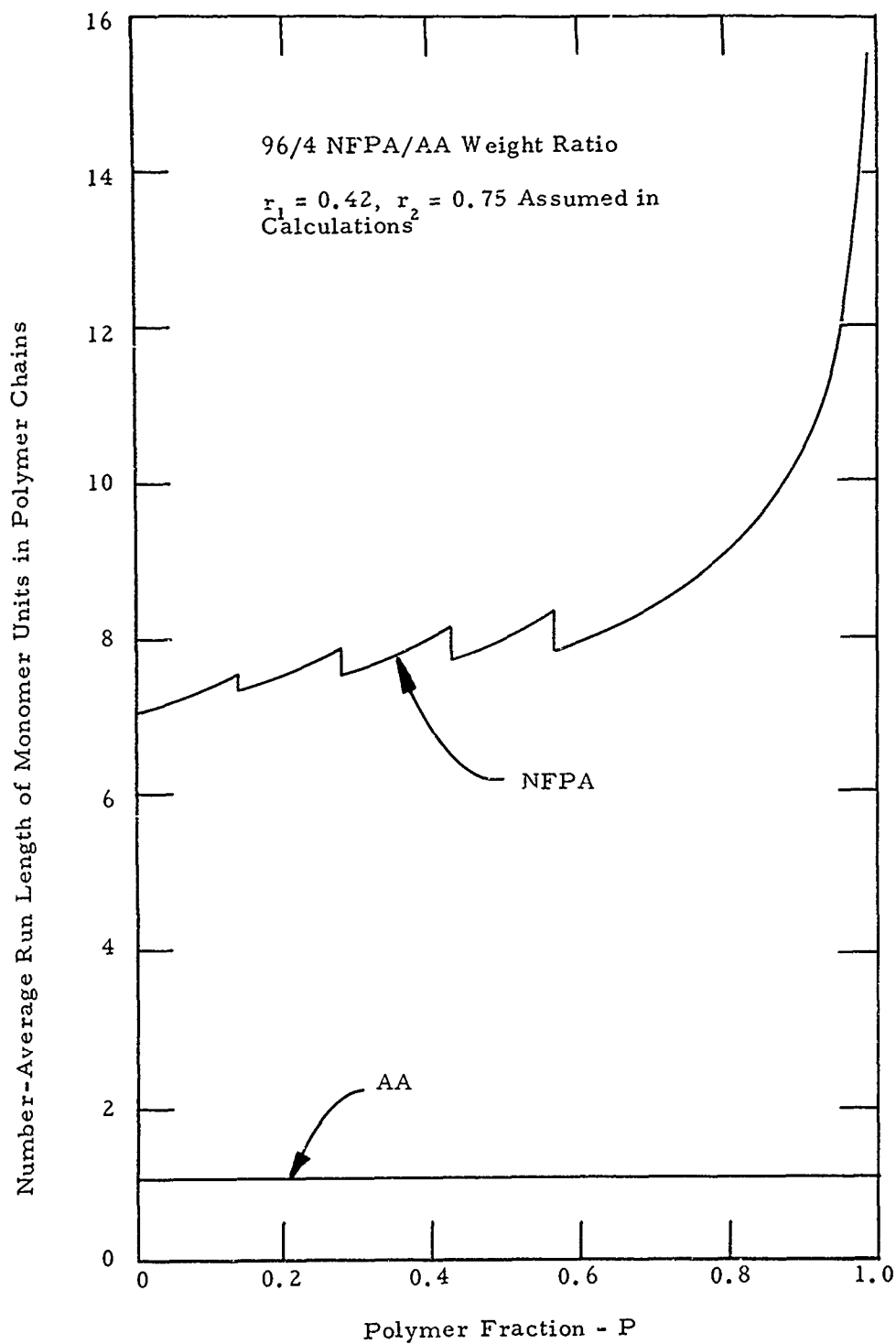
Fig. 36 Number-Average Monomer Run Lengths in Polymer, 39%-IAP

9.0 CONCLUSIONS

1. A new process for making the copolymer has been developed which has a high reactor productivity, which results in readily processable RH-SE-103 propellant slurries, and which yields a propellant with superior physical properties and thermal stability.

2. Additional data are needed to conform the high-temperature mechanical-property stability which was indicated in the preliminary data. If additional experiments confirm the preliminary results, RH-SE-103 propellant made with the new copolymer appears ready for immediate use in missile systems without additional development.

3. Mathematical models for the compositional uniformity and polymerization rate of the copolymer have been obtained and demonstrated. Additional qualitative models for molecular weight and molecular-weight distribution have been obtained which are useful in gaining an insight into the copolymerization processes discussed above. These models were used in developing the IAP to make co-polymer for RH-SE-103 propellant, and they should be very useful if similar work is required for other propellants.

4. The NFPA/AA copolymer molecular weight has been shown to have large effects on propellant physical properties and processing characteristics.

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11.0   APPENDIX. GAS-CHROMATOGRAPHIC-ANALYSIS PROCEDURES

Typically GC analyses are obtained by relating an unknown concentration to that of an internal standard material having a known concentration. However, this procedure has several drawbacks in analyzing monomer concentrations in EtOAc or other volatile solvents. Frequently suitable internal standard compounds evaporate so quickly that appreciable errors are made in weighing small amounts of standard to the sample. If the standard compound is added to the reactor prior to the reaction this problem is overcome, but the standard material could possibly exert an unknown influence on the reaction.

In order to overcome these difficulties, an absolute calibration procedure was used which related area under the GC output curve to the absolute quantity of monomer in the sample injected in the GC. Samples containing various carefully weighed amounts of EtOAc, NFPA, and AA were made up and the densities of these samples were accurately measured. By use of a Chaney[1] adapter on a microliter syringe, it was possible to inject accurately known volumes of sample into the GC apparatus. The areas under the GC peaks were corrected for base-line drift, and calibration charts were constructed in which the corrected area was plotted against the mass of monomer. The calibration chart for NFPA monomer is shown in Fig. 37, and the chart for AA monomer is shown in Fig. 38.

All density measurements were made at 30°C although the samples were injected into the GC apparatus at room temperature which was held at approximately 25°C. These density measurements were required in order to obtain the mass of the known volume of sample injected into the GC apparatus.

The GC column was constructed from a 3-ft length of 1/4-in. O.D. tubing packed with 90-100 American standard mesh Anakrom ABS® [*] covered with 20% disodecylphthalate. A helium flow rate of

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[1] Hamilton Company, Whittier, California
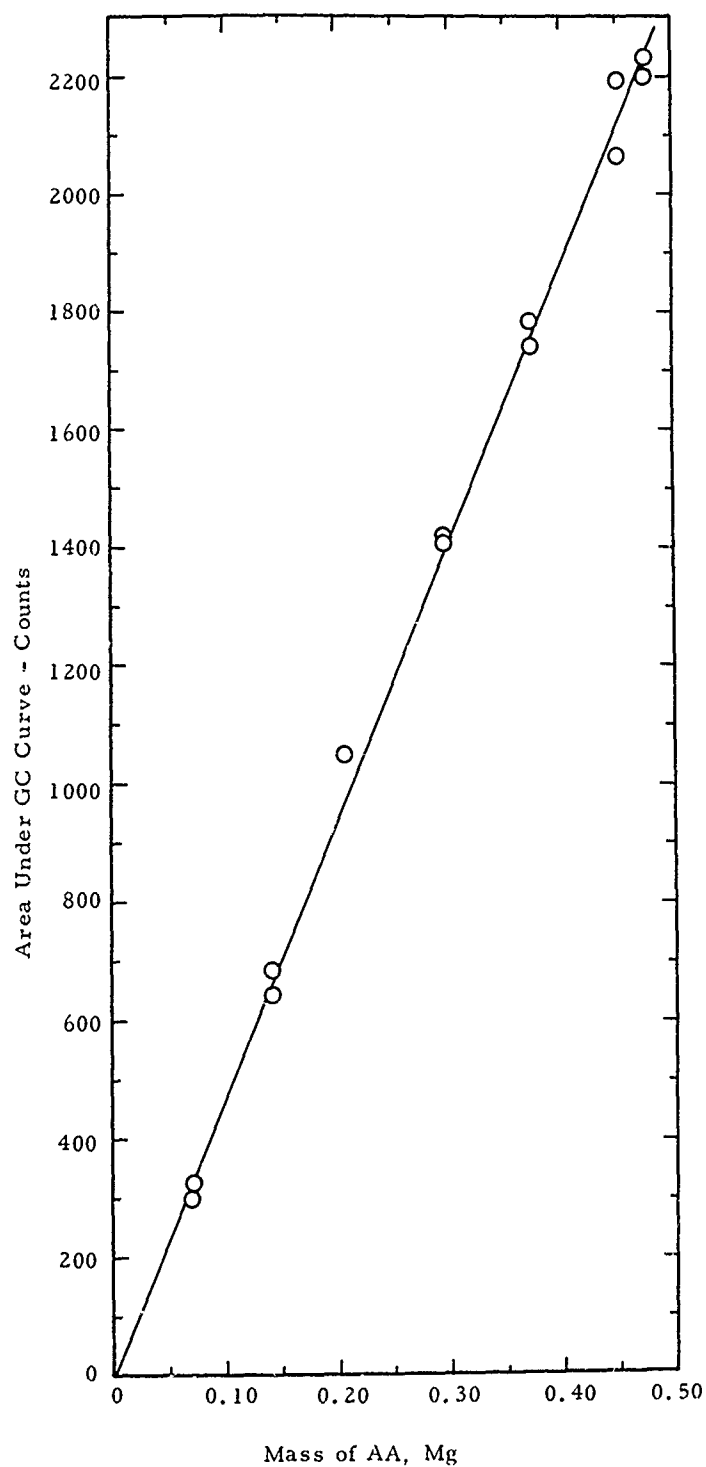[*] Trademark of Analabs, Inc., 7 Hobson Avenue, Hamden, Conn.

Fig. 37 GC-Calibration Chart for AA
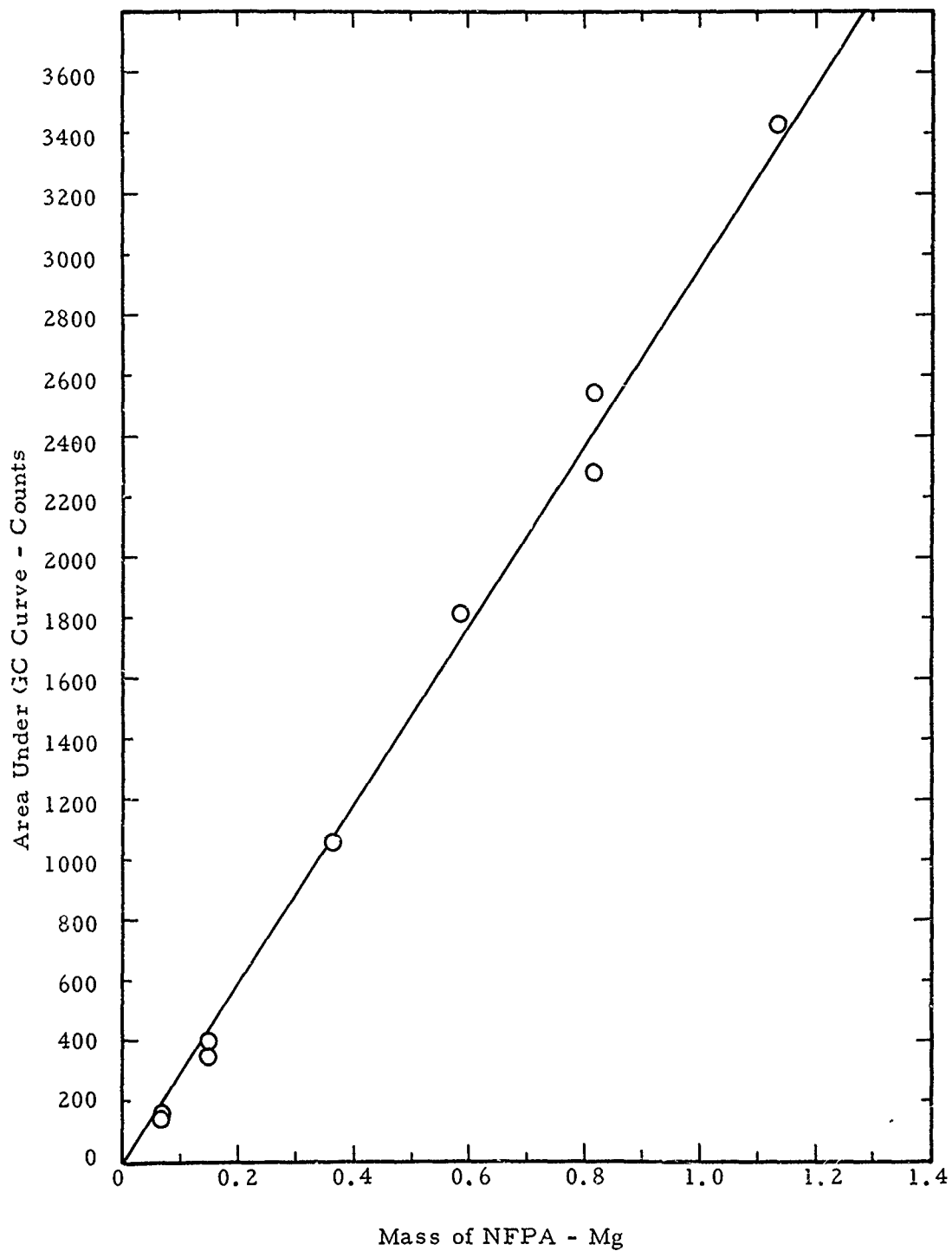
Fig. 38 GC-Calibration Chart for NFPA

56 ml/min was maintained and the column temperature was held at
80°C ± 1°C. Column temperature was a critical factor and many GC
traces were discarded due to improper temperature control. The
oven available for this work was not the most modern that can be
obtained, and the temperature control system originally on the oven was
unsatisfactory because it allowed a large temperature cycle to occur.
Satisfactory control was obtained by removing the on-off controller
and adjusting the power setting on the oven so that the desired tempera-
ture was indicated on the oven temperature dial. (Temperatures
throughout the oven were measured with thermocouples and a potentiometer
and these results confirmed the dial reading.)

In preliminary testing, it was found that 4-cc vials with
polyethylene snap-in caps would lose only a negligible percentage
of the sample by evaporation if the vials were nearly full. Vials
which contained a small amount of sample exhibited a greater per-
centage loss, although the absolute loss was approximately the same.
The samples were inhibited by adding a small amount of diphenyl-
picrylhydrazyl to the vial, and they were stored in the dark at a
temperature of 40°F. The GC traces were obtained the next day.
The 40°F temperature was felt to be the best temperature for storage
because it was cold enough to minimize evaporation, but not cold
enough for the AA to freeze and possibly dimerize on melting.

A word of caution is appropriate for anyone considering the
use of rubber syringe caps for sample vials containing volatile com-
ponents. It was observed in preliminary evaporation tests that rubber
syringe caps absorbed a great deal of the sample from the vial as
indicated by the cap weight gain. The phenomenon occurred without
the cap coming in contact with the liquid phase of the sample.

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13 ABSTRACT

(U) This report discusses continued efforts to improve the process for making NFPA-acrylic acid copolymers and to characterize the product. Particular emphasis is directed toward developing, experimentally testing, and utilizing mathematical models of the process. The scope of the work includes considerations of compositional uniformity, molecular-weight distribution, and polymerization rate of the copolymer. A new process whereby the comonomers are added incrementally is described which greatly increases the productivity of the reactor and permits control of molecular weight. Propellant made from copolymer prepared in this manner has improved physical properties, fissuring characteristics, and physical-property aging characteristics.

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